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# POTENTIOMETRIC TITRATIONS

## A THEORETICAL AND PRACTICAL TREATISE

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# POTENTIOMETRIC TITRATIONS

## A THEORETICAL AND PRACTICAL TREATISE

BY

DR. I. M. KOLTHOFF

*Conservator of the Pharmaceutical Laboratory of the State University of Utrecht, Holland*

AND

N. HOWELL FURMAN, PH.D.

*Assistant Professor of Chemistry, Princeton University, Princeton, N. J.*

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# PREFACE

Electrometric titrations may be divided into two classes:

*a.* Conductometric Titrations, in which the end-point is detected by measuring the change of electrical conductance during the titration and plotting the value thus obtained on a graph. For details the reader is referred to the monograph of I. M. Kolthoff, "Die Konduktometrischen Titrationen," published by Th. Steinkopf, Dresden, 1923.

*b.* Potentiometric Titrations, in which the end-point is detected by measuring the change in potential of a suitable electrode during the titration.

There is a very great difference between the principles upon which the two methods are based, and therefore it is not entirely correct to refer to either of the two methods by the general name "electrometric titration," as is often done. (*Cf.* Erich Müller, "Die Elektrometrische Massanalyse.") In order to avoid confusion, the authors hope that in the future the names "potentiometric" and "conductometric" titrations will be generally adopted. In this book they will discuss only potentiometric titrations.

It is their intention to attempt to make the theoretical considerations as general as possible. Therefore all oxidation-reduction reactions have been discussed on a common basis with other reactions so that one may work with them from the standpoint of the law of mass action. The advantage thereby gained is that all of the equations are of importance not only for potentiometric systems, but are also of equal value for ordinary titrations. For this reason a full treatment of reaction constants and of the change of ion concentrations in the vicinity of the

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equivalence-point (usually called, incorrectly, the end-point) is given in the first three chapters. If we know the sensitivity of an indicator for any special ion which is under consideration, it is very easy to calculate the accuracy of the titration—or the titration error—in any case.

In Chapters IV and V the authors apply the material of the preceding chapters to potentiometric titrations. The reader will also find there a mathematical discussion of the change of the ion exponent and electrode potential in the neighborhood of the equivalence-point. The authors are indebted to Dr. A. L. Th. Moesveld of the van't Hoff Laboratory, Utrecht (Holland), for his aid in the derivation of these equations. They wish to emphasize the fact that the mathematical discussion is of more theoretical than practical importance. They have considered it of importance to develop the mathematical side of the question in the interest of clearer understanding of what occurs near the end-point, and also for the exact calculation of the titration error.

Part II, which deals with practical applications, is divided into two parts:

The first part contains a general description of the technique of potentiometric titrations. The authors are indebted for many valuable details to the excellent book, " The Determination of Hydrogen Ions," by W. M. Clark (Baltimore, 1922), and to " Die Elektrometrische Massanalyse," by Erich Müller, (2d Ed., Steinkopf, Dresden, 1923).

In the chapters dealing with special determinations, the authors have described the reactions to which the potentiometric method is applicable. Especial attention is called to the general part, which treats the following topics: the electrode material; characteristics of electrodes; influence of foreign substances, and of temperature, on the titration curve.

For minute details the reader is referred to the original literature concerning potentiometric titrations. The authors have attempted to make full acknowledgment of the use of this literature. They will be glad to have their attention called to any gaps in their list of literature references.

They hope they have shown in this book that analytical chemistry is not merely an empirical branch of the subject, rendering servile assistance to the whole, but that it is rather a science in itself, for the rational development of which a thorough understanding of physico-chemical principles is necessary.

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# POTENTIOMETRIC TITRATIONS

## PART I

## FUNDAMENTAL PRINCIPLES

## CHAPTER I

## PRINCIPLES OF PRECIPITATION AND NEUTRALIZATION REACTIONS

**1. Ions and Ionic Reactions.**—In the study of potentiometric titrations we are constantly dealing with the reactions of ions. As is well known, electrolytes may be classified as strong and weak. According to the theory of Arrhenius, strong electrolytes in solution are in the main dissociated into their ions. The **degree of dissociation,** i.e., the portion of 1 gram mole that is dissociated, decreases with increasing concentration of the electrolyte. According to the more modern conceptions of Bjerrum and Debye, strong electrolytes are completely dissociated. Owing to interionic forces, however, the *activity* of the ions decreases with increasing concentration of the electrolyte. Although the latter theory is in closer accord with the facts, it is not necessary for the student of potentiometric titrations to adhere rigidly to either, since it will suffice for his purpose to assume that strong electrolytes are completely dissociated in all concentrations (Arrhenius) or that the ions have unit activity (Bjerrum). The authors are fully conscious of the small error in this assumption, and choose to disregard it because it is without influence upon the theoretical treatment of potentiometric titrations. Hence, if we consider a 0.1 molar solution of a strong electrolyte BA, we have:

$$[B^+] = [A^-] = 0.1 = 10^{-1},$$

in which the brackets represent concentration. $[B^+]$ is the cation concentration; $[A^-]$ is the anion concentration. Instead of expressing the ion concentration as such, the authors will often designate it by another term, which was first proposed by S. P. L. Sörensen, viz., the **ion exponent,** $p_I$. The ion exponent is the negative logarithm of the ion concentration. Therefore:

$$p_I = -\log [I] = \frac{1}{\log [I]}.$$

This mode of expression is of great practical advantage. During the course of a titration the ion concentration changes over a considerable range. Let us consider, for example, the titration of 0.1 N silver nitrate solution with potassium iodide. In this case the silver-ion concentration changes from $10^{-1}$ N to $10^{-15}$ N, if the iodide concentration is $10^{-1}$ N at the end. Hence the silver-ion concentration decreases $10^{14}$ fold during the titration. Now, if we should wish to represent graphically the course of the titration as a function of the amount of reagent, it would be practically impossible to choose the unit of concentration in such a way that we could present the whole course. If, however, we express the ion concentration by the ion exponent, we have in this instance a change in $p_{Ag^+}$ from 1 to 15, i.e., an increase of 14 units. As the ion exponent is the negative logarithm of the concentration, it increases with decreasing concentration. We must bear in mind the fact that a small error made in the determination of the ion exponent is magnified many times when we express the result in ion concentration. For example:

$$p_{Ag^+} = 4.0 \qquad [Ag^+] = 10 \times 10^{-5}$$

$$p_{Ag^+} = 4.1 \qquad [Ag^+] = 8 \times 10^{-5}$$

A difference of 0.1 in $p_{Ag}$, in this example, corresponds to a 20 per cent difference in the ion concentration.

For the purpose of the present discussion, we may distinguish two classes of ionic reactions:

*Combinations of Ions.*—A cation combines with an anion to form a slightly soluble, a slightly dissociated, or a complex compound:

$Ag^+ + Cl^- \rightleftarrows AgCl$ (slightly soluble)
$H^+ + OH^- \rightleftarrows H_2O$ (slight dissociated)
$Ag^+ \quad 2CN^- \rightleftarrows Ag(CN)_2^-$ (complex)

*Oxidation-reduction Reactions.*—An ion is reduced when it takes up one or more electrons, or it is oxidized when it gives off one or more electrons:

$Fe^{+++} + \ominus \rightleftarrows Fe^{++}$ (reduction of ferric ion)
$Fe^{++} \rightleftarrows Fe^{+++} + \ominus$ (oxidation of ferrous ion)

A detailed discussion of the various reactions will be given in Part II.

**2. Precipitation Reactions and Solubility Product.**—The occurrence of a precipitation reaction may be represented by the equation:

$$B^+ + A^- \rightleftarrows BA,$$

if both ions are univalent. BA is a slightly soluble substance. Since the reaction is reversible, we may apply the law of mass action and write the expression:

$$\frac{[B^+][A^-]}{[BA]} = K. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[BA] represents the concentration of the undissociated part of the slightly soluble substance. Its value is constant at any definite temperature. Hence, we may write in place of equation (1):

$$[B^+][A^-] = S. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

S represents the **solubility product.** If the product of $[B^+]$ and $[A^-]$ is larger than this value, the salt BA will precipitate. In a saturated solution of the salt BA, we may assume that all of the salt is electrolytically dissociated into its ions; and since there are equivalent quantities of anion and cation in the solution,

$$[B^+] = [A^-] = c. \quad \dots\dots\dots \quad (3)$$

if $c$ represents the solubility of BA. And, further, from (1) and (2):

$$[B^+]^2 = [A^-]^2 = c^2 = S. \quad \dots\dots \quad (4)$$

Instead of working with the ion concentrations, it is usually of advantage to express the relation in terms of ion exponents. Then we have:

$$p_B + p_A = p_S. \quad \dots\dots\dots \quad (5)$$

$p_S$ is the negative logarithm of the solubility product. It will be called the **solubility exponent.** In a saturated solution

$$p_B = p_A = \tfrac{1}{2}p_S. \quad \dots\dots \quad (6)$$

When we have BA in contact with an excess of $B^+$ or $A^-$, we may readily calculate the unknown ion concentration. It follows from (2) that:

$$[B^+] = \frac{S}{[A^-]} \quad (7), \quad \text{and} \quad [A^-] = \frac{S}{[B^+]}, \quad \dots \quad (8)$$

and from (5) that:

$$p_B = p_S - p_A. \quad \dots\dots \quad (9)$$

$$p_A = p_S - p_B. \quad \dots\dots \quad (10)$$

*Example.*—Let us assume that S is equal to $10^{-10}$ or that $p_S$ equals 10, which is the case with silver chloride. Hence in a saturated solution:

$$[Ag^+] = [Cl^-] = \sqrt{10^{-10}} = 10^{-5}.$$

The solubility of silver chloride is $10^{-5}$. In the solution we have:

$$p_{Ag} = p_{Cl} = \tfrac{1}{2}p_S = 5.$$

If the silver chloride is in contact with a solution of silver-ion concentration $10^{-3}(p_{Ag} = 3)$, we have, according to equation (8):

$$[Cl^-] = \frac{10^{-10}}{10^{-3}} = 10^{-7},$$

or

$$p_{Cl} = 10 - 3 = 7.$$

If there is an excess of $B^+$, then $[A^-]$ corresponds to the solubility of BA since the latter is completely dissociated in solution.

We see therefore that the solubility decreases with increasing excess of one of the ions. Its value is a maximum in pure saturated solution. When $[B^+]$, for example, is 10 times greater than in the pure saturated solution, $[A^-]$ is 10 times smaller and therefore the solubility is also decreased tenfold. If we add an excess of one of the ions to a saturated solution of BA, it is not always permissible to assume that the total concentration of this ion is equal to the concentration that we add. In making this assumption we are neglecting the solubility of BA. It is very simple, however, to calculate the concentrations of both ions when the excess is known. If we add so much of a solution of $B^+$-ions that the concentration of these ions is $b$, then the total concentration of $B^+$ is equal to $b + x$, where $x$ represents the solubility of BA. In this case $[A^-]$ is equal to $x$. Then we have:

$$(b + x)x = S. \qquad (11)$$

$$x^2 + bx - S = 0.$$

$$x = -\frac{b}{2} + \sqrt{\frac{b^2}{4} + S}. \qquad (12)$$

From this equation it may be deduced that $x$ becomes smaller as $b$ increases or as S decreases. In most practical cases we may calculate that $[B^+]$ is equal to $b$, and that $x$ is negligible in comparison with $b$; but this is not always permissible. In the following table the authors give some values of $x$ that correspond to known values of $b$ and S.

TABLE A

| $S=10^{-6}$ | | $S=10^{-8}$ | | $S=10^{-10}$ | |
|---|---|---|---|---|---|
| $b$ | $x=[A^-]$ | $b$ | $x=[A^-]$ | $b$ | $x=[A^-]$ |
| $1\times10^{-3}$ | $6.2\times10^{-4}$ | $1\times10^{-4}$ | $6.2\times10^{-5}$ | $1\times10^{-4}$ | $1\times10^{-6}$ |
| $2\times10^{-3}$ | $4\times10^{-4}$ | $2\times10^{-4}$ | $4\times10^{-5}$ | $2\times10^{-4}$ | $5\times10^{-7}$ |
| $5\times10^{-3}$ | $2\times10^{-4}$ | $5\times10^{-4}$ | $2\times10^{-5}$ | $5\times10^{-4}$ | $2\times10^{-7}$ |
| $10\times10^{-3}$ | $1\times10^{-4}$ | $10\times10^{-4}$ | $1\times10^{-5}$ | $10\times10^{-4}$ | $1\times10^{-7}$ |

In the next section it will be shown that these considerations are of great importance in calculating the titration error at the equivalence-point. If, for example, we have a substance with a solubility product of $10^{-6}$, and if we add to 100 cc. of the saturated solution 1 cc. of 0.1 N solution of $B^+$, then $b = 1 \times 10^{-3}$. $[A^-]$ was originally equal to $10^{-3}$ N in the saturated solution; by the addition of the excess of $B^+$ it is decreased to $6.2 \times 10^{-4}$; hence $[A^-]$ has become only 1.6 times smaller. We get the same ratio if we add 0.1 cc. of 0.1 N solution of $B^+$ to 100 cc. of a saturated solution of a substance with a solubility product of $10^{-8}$. As we shall see further on, the accuracy of a titration is dependent upon the changes in ion concentrations in close proximity to the saturation point (equivalence-point).

Thus far we have considered only the case of two univalent ions that react to form the slightly soluble substances BA. The matter is more complicated if a univalent ion reacts with a bivalent ion to form the insoluble salt:

$$2B^+ + A^= \rightleftarrows B_2A,$$

or

$$B^{++} + 2A^- \rightleftarrows BA_2.$$

We shall consider only the former of the two equations, since the latter is precisely similar. By applying the law of mass action we find:

$$[B^+]^2[A^=] = S_{B_2A}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

In the saturated solution we have twice as many $B^+$- as $A^=$-ions; hence:

$$[B^+] = 2[A^=],$$

and

$$\tfrac{1}{2}[B^+]^3 = 4[A^=]^3 = S_{B_2A}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If the solubility of $B_2A$, expressed in moles per liter, is $c$, we have:

$$c = [A^=],$$

and from (14) we have:

$$c = \sqrt[3]{\frac{S_{B_2A}}{4}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

if we express the relations in ion exponents we have:

$$2p_B + p_A = p_S. \qquad (16)$$

In a saturated solution of $B_2A$ we have:

$$p_B = p_A - \log 2 = p_A - 0.30, \qquad (17)$$

and

$$3p_B + 0.30 = p_S. \qquad (18)$$

When we have $B_2A$ in contact with an excess of $B^+$ or $A^=$, we may calculate the concentration of the unknown ion by means of the equations:

$$[B^+] = \sqrt{\frac{S_{B_2A}}{[A^=]}}. \qquad (19)$$

$$[A^=] = \frac{S_{B_2A}}{[B^+]^2}. \qquad (20)$$

From equation (16) it may be deduced that:

$$p_B = \frac{p_S - p_A}{2}. \qquad (21)$$

$$p_A = p_S - 2p_B.$$

*Illustration.*—Let us assume that S is equal to $10^{-12}$, or $p_S$ to 12, which is very nearly the case with silver oxalate.

In a saturated solution we have:

$$[B^+] = \sqrt[3]{2S_{B_2A}} = \sqrt[3]{2 \times 10^{-12}} = 10^{-3.9} = 1.26 \times 10^{-4},$$

and

$$[A^=] = \tfrac{1}{2}[B^+] = 0.63 \times 10^{-4}.$$

If we apply equation (18) we find immediately that:

$$p_B = \frac{p_S - 0.30}{3} = 3.9,$$

and

$$p_A = 4.2, \quad (17).$$

The solubility is at a maximum in the saturated solution of the pure substance, and decreases with increasing concentration of either of the ions. The relation between the solubility and the excess of either of the ions is more complicated than when we are dealing with a uni-univalent substance, BA. If, for example, the concentration of the $B^+$-ions is 10 times larger than in the saturated solution, it follows from equation (13) that both $[A^=]$ and the solubility are 100 times less. If, on the other hand, $[A^=]$ is 10 times larger than in the saturated solution, $[B^+]$ has become only $\sqrt{10} = 3.2$ times smaller, and the solubility has decreased 6.4 times.

If we add an excess of one of the ions to a saturated solution of $B_2A$, then the total concentration of this ion is larger than that corresponding to the amount added, owing to the solubility of the substance. If the latter is $x$-molar under these special conditions, then the concentration of B-ions is $2x$, and that of A-ions is $x$. Now let us assume that we have added an excess of $B^+$ corresponding to a concentration $b$. In this case the total concentration of $B^+$ is $(b + 2x)$ and that of $A^=$ is equal to $x$. According to equation (13) we have:

$$(b + 2x)^2 x = S_{B_2A},$$

or

$$4x^3 + 4bx^2 + b^2x - S_{B_2A} = 0. \quad . \quad . \quad . \quad . \quad (23)$$

It is rather difficult to solve this equation for $x$, and, when we have a number of cases to calculate, much time is consumed. It is much easier to use a graph in which the value of $x$ is plotted against different values of $[B^+]$ and $[A^=]$. From the foregoing it is evident that with the aid of equation (13) we may readily calculate the values of $[A^=]$ (i.e., $x$) that belong to different concentrations of $B^+$. Conversely, we may calculate the values of $[B^+]$ (i.e., $2x$) that belong to various concentrations of $A^=$.

This has been done in Figs. 1 and 2. In this example $S_{B_2A}$ has been taken equal to $10^{-12}$. The abscissas are the values of $x$ belonging to the concentrations of $B^+$ (or of $A^=$ in Fig. 2) that are plotted as ordinates. Now let us assume that we add a known excess of $B^+$, corresponding to a concentration of $b$, to a solution which is in contact with $B_2A$. Then we first reckon that $[B^+]$ is equal to $b + c$ and look up the value of $x$ belonging to this $[B^+]$. ($c$ is the concentration of B in the saturated solution of $B_2A$.)

If this method were correct, then $[B^+]$ should be equal to $b + 2x$. But this value is too high because we have neglected the decrease of the solubility, and a value $x'$, smaller than $x$, should be used. We now put $b + 2x'$ in place of $[B^+]$, and find a corresponding value $x''$. The correct value of $[B^+]$ can usually be found by means of one or two interpolations. It is

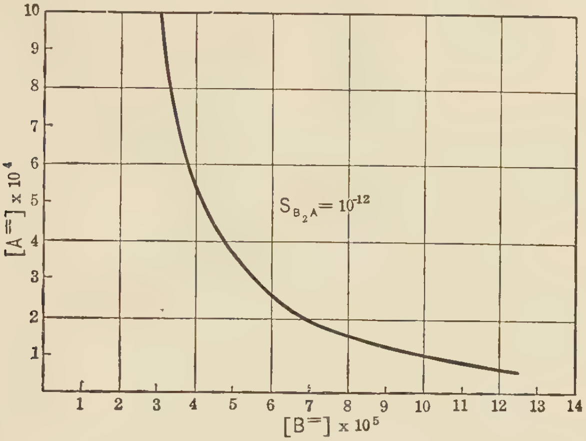

FIG. 1.—Excess of $[B^+]$. $[A^-] \times 10^5$ = Solubility $\times 10^5$. S corresponds to saturated solution.

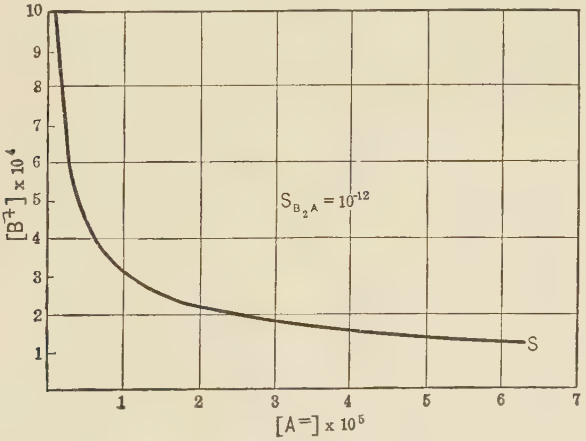

FIG. 2.—Excess of $[A^-]$.

easier to make a new curve, derived directly from Fig. 1, in which values of $[B^+]$ are plotted against the corresponding values of $b$. From Fig. 1 we see, for example, that a value of $[B^+] = 2.95 \times 10^{-4}$ is linked with an $[A^=]$ value of $1 \times 10^{-5}$. Hence the value $[B^+] = 2.95 \times 10^{-4}$ corresponds to $b = 2.95 \times 10^{-4} - 2 \times 10^{-5} = 2.75 \times 10^{-4}$, etc. In the following table are given values of $[B^+]$ and $[A^=]$ belonging to a known excess $b$ of B-ions, or $a$ of A-ions.

TABLE B

SOLUBILITY PRODUCT OF $B_2A = 10^{-12}$. EXCESS $b$ OF $[B^+]$

| $b$ | $[B^+]$ | $[A^=]$ | Solubility of $B_2A$ |
|---|---|---|---|
| 0 | $1.26 \times 10^{-4}$ | $6.3 \times 10^{-5}$ | $6.3 \times 10^{-5}$ (saturated solution) |
| $1 \times 10^{-4}$ | $1.75 \times 10^{-4}$ | $3.75 \times 10^{-5}$ | $3.75 \times 10^{-5}$ |
| $2 \times 10^{-4}$ | $2.35 \times 10^{-4}$ | $1.75 \times 10^{-5}$ | $1.75 \times 10^{-5}$ |
| $3 \times 10^{-4}$ | $3.2 \times 10^{-4}$ | $1 \times 10^{-5}$ | $1 \times 10^{-5}$ |
| $5 \times 10^{-4}$ | $5.08 \times 10^{-4}$ | $0.4 \times 10^{-5}$ | $0.4 \times 10^{-5}$ |

SOLUBILITY PRODUCT OF $B_2A = 10^{-12}$. EXCESS $a$ OF $[A^=]$

| $a$ | $[B^+]$ | $[A^=]$ | Solubility of $B_2A$ |
|---|---|---|---|
| 0 | $1.26 \times 10^{-4}$ | $6.3 \times 10^{-5}$ | $6.3 \times 10^{-5}$ |
| $0.5 \times 10^{-4}$ | $1 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | $5 \times 10^{-5}$ |
| $1 \times 10^{-4}$ | $8.4 \times 10^{-5}$ | $1.42 \times 10^{-4}$ | $4.2 \times 10^{-5}$ |
| $2 \times 10^{-4}$ | $6.4 \times 10^{-5}$ | $2.32 \times 10^{-4}$ | $3.2 \times 10^{-5}$ |
| $3 \times 10^{-4}$ | $5.4 \times 10^{-5}$ | $3.27 \times 10^{-4}$ | $2.7 \times 10^{-5}$ |
| $5 \times 10^{-4}$ | $4.2 \times 10^{-5}$ | $5.21 \times 10^{-4}$ | $2.1 \times 10^{-5}$ |
| $10 \times 10^{-4}$ | $3.2 \times 10^{-5}$ | $10.16 \times 10^{-4}$ | $1.6 \times 10^{-5}$ |

As we shall see later, in the discussion of titration curves, it is of great importance to know the variation of the ion concentration in the neighborhood of the equivalence-point. From the figures (1 and 2) we see that the decrease in $[A^=]$ and in the solubility of $B_2A$ caused by an excess of B-ions is much greater than the decrease in $[B^+]$ and in the solubility of $B_2A$ caused by an excess of A-ions. Moreover, as we can see from the figures, it is of practical importance to know:

*First.*—In what cases we may neglect the solubility, i.e., when we may put $[B^+]$ equal to $b$, or $[A^=]$ equal to $a$.

*Second.*—How great is the solubility with a known excess of $B^+$ or $A^=$. In many cases when the solubility of $B_2A$ is rather large, a direct titration does not give good results. In such cases we may add an excess of one of the precipitating ions, and determine the excess in the filtrate. By means of the above considerations we are able to calculate the solubility of $B_2A$ under the conditions with which we are working, and hence we can calculate the error caused by the solubility.

In cases where the slightly soluble substance has the composition $BA_2$, in which B is the bivalent cation, we may apply the calculations given above. The only difference is that the concentrations that were calculated for $B^+$ now apply to $A^-$, and, conversely, the values for $A^=$ now apply to $B^{++}$.

In general, when the precipitate has the composition BA, in which $B^{n+}$ and $A^{n-}$ are multivalent ions of the same valence, we may apply the same formulas that were used for the substance BA, which was formed by univalent ions. If, however, the composition is $B_xA_y$, in which B and A are multivalent ions of different valences, the calculations become very complicated. We get equations of higher order which are very difficult or impossible to solve. In these cases the graphical method always gives a simple solution of the change in ion concentration with known excess of one of the ions.

The precipitation of the salt $B_xA_y$ may be represented by the equation:

$$xB^{n+} + yA^{m-} \rightleftarrows B_xA_y;$$

$n$ is the valence of the cation, $m$ that of the anion.

According to the law of mass action, we have:

$$[B^{n+}]^x[A^{m-}]^y = S_{B_xA_y}, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and the relation between $[B^{n+}]$ and $[A^{-m}]$ is:

$$[B^{n+}] = \sqrt[x]{\frac{S_{B_xA_y}}{[A^{m-}]^y}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

$$[A^{m-}] = \sqrt[y]{\frac{S_{B_xA_y}}{[B^{n+}]^x}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Instead of working with the ion concentrations, it is much easier in this case to use the ion exponents. From equation (24) we find:

$$xp_{\mathrm{B}} + yp_{\mathrm{A}} = p_{\mathrm{S}}. \quad \ldots\ldots \quad (27)$$

$$p_{\mathrm{B}} = \frac{p_{\mathrm{S}} - yp_{\mathrm{A}}}{x}. \quad \ldots\ldots \quad (28)$$

$$p_{\mathrm{A}} = \frac{p_{\mathrm{S}} - xp_{\mathrm{B}}}{y}. \quad \ldots\ldots \quad (29)$$

When $[\mathrm{B}^{n+}]$ or $p_{\mathrm{B}}$ is known we may readily calculate the concentration of $\mathrm{A}^{m-}$ and the corresponding solubility. If we decrease $[\mathrm{B}^{n+}]$ by the B-ion concentration that is due to the solubility, we have the excess, $b$, added to a saturated solution of $\mathrm{B}_x\mathrm{A}_y$. Then we can plot $b$ against $[\mathrm{B}^{n+}]$ or $[\mathrm{A}^{m-}]$ in a graph, and from this we can read off the change in ion concentration upon the addition of an excess of A- or B-ions to a saturated solution of $\mathrm{B}_x\mathrm{A}_y$.

In the saturated solution of the substance $\mathrm{B}_x\mathrm{A}_y$ we have $y$ moles of $\mathrm{A}^{m-}$ per $x$ moles of $\mathrm{B}^{n+}$. Therefore:

$$[\mathrm{B}^{n+}] = \frac{x}{y}[\mathrm{A}^{m-}],$$

and

$$[\mathrm{A}^{m-}] = \frac{y}{x}[\mathrm{B}^{n+}].$$

Combining these values with equations (25) to (29), we have in the saturated solution:

$$[\mathrm{B}^{n+}] = \sqrt[x+y]{\left(\frac{x}{y}\right)^{y} S_{\mathrm{B}_x\mathrm{A}_y}}, \quad \ldots\ldots \quad (25a)$$

$$[\mathrm{A}^{m-}] = \sqrt[x+y]{\left(\frac{y}{x}\right)^{x} S_{\mathrm{B}_x\mathrm{A}_y}}, \quad \ldots\ldots \quad (26a)$$

and

$$p_{\mathrm{B}} = \frac{1}{x+y}\left(p_{\mathrm{S}} - y\log\frac{x}{y}\right), \quad \ldots \quad (28a)$$

$$p_{\mathrm{A}} = \frac{1}{x+y}\left(p_{\mathrm{S}} - x\log\frac{y}{x}\right). \quad \ldots \quad (29a)$$

**3. Presence of Two Ions That Form Insoluble Compounds with the Same Ion.**—If we have two ions, $A^-$ and $A_1^-$, both of which form insoluble salts, BA and $BA_1$, with the cation $B^+$, we are able to calculate what will happen upon adding a solution of $B^+$ to a mixture of the two anions. From the preceding paragraph we see that:

$$[B^+][A^-] = S_{BA},$$

$$[B^+][A_1^-] = S_{BA_1}.$$

Now let us assume that we have added $B^+$ until both BA and $BA_1$ are present as solid phases. Then, according to the equations, we have:

$$[B^+] = \frac{S_{BA}}{[A^-]} = \frac{S_{BA_1}}{[A_1^-]},$$

or

$$\frac{[A_1^-]}{[A^-]} = \frac{S_{BA_1}}{S_{BA}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Hence, in this case, the ratio between the concentrations of the two ions is the same as that between the solubility products of the two salts. It is of importance, for our purposes, to know under what conditions one of the two salts may be practically completely precipitated free from the other. Only when this condition is fulfilled may we titrate the ion $A_1^-$ in the presence of $A^-$. From equation (30) it is evident that the insoluble salt BA can not be formed when

$$\frac{[A_1^-]}{[A^-]} > \frac{S_{BA_1}}{S_{BA}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

Hence, if we assume that $BA_1$ is the less soluble of the two compounds, pure $BA_1$ will be precipitated from a mixture of $A_1$- and A-ions by the addition of B-ions until we reach the conditions that are expressed in the equation. From this point $BA_1$ and BA are precipitated simultaneously.

*Illustration.*—We wish to titrate a mixture of iodide and chloride ions with silver ion. In this case AgI alone will be precipitated until the ratio of the ions is:

$$\frac{[I^-]}{[Cl^-]} = \frac{S_{AgI}}{S_{AgCl}} = \frac{10^{-16}}{10^{-10}} = 10^{-6}.$$

When the iodide concentration has become one million times smaller than the chloride-ion concentration, a further addition of silver ions will cause a precipitation of silver chloride. Before this point, however, silver iodide alone is formed. We may conclude from the figures given that a quantitative precipitation of AgI occurs in the presence of chloride, even when the latter concentration is originally 100 times greater, for example, than that of the iodide. In this instance the iodide concentration becomes 10,000 times smaller than its original value before the precipitation of AgCl begins, and the separation is therefore quantitative.

If, on the other hand, we have a mixture of $Br^-$ and $Cl^-$, silver bromide alone will be precipitated until:

$$\frac{[Br^-]}{[Cl^-]} = \frac{S_{AgBr}}{S_{AgCl}} = 6 \times 10^{-3}.$$

Here the conditions are far less favorable for a quantitative separation than in the case of $I^-$ and $Cl^-$. This question will be discussed in greater detail in Part II, which deals with Practical Applications. (*Cf.* Chapter IX.)

It is necessary to know the change in ion concentration near the point where the precipitation of the second salt, BA, begins, in order to determine the accuracy of a titration. We may apply here the same kind of equations as we did in § 2. Usually, however, the calculation may be made in a very simple manner. In cases where a titration of $A_1^-$ in the presence of $A^-$ is possible, we may assume that $[A_1^-]$—before the precipitation point of BA is reached—is equal to the total excess of $A_1$-ions in the solution. Theoretically, we should add to this value the concentration of $A_1$-ions that is due to the solubility of $BA_1$, but in instances where a quantitative separation is possible we may neglect the latter value. When the precipitation point of

BA has been reached, a continued addition of B-ions will change the ion concentrations very little. Practically all of the B-ions will be used in the formation of BA; and as there is a large excess of A-ions, the removal of a small portion will not have much influence on the total A-ion concentration. When almost all of the A-ions have been precipitated there is a sharp change in the ion concentration, as pointed out in § 2.

*Summary.*—In the titration of a mixture of $A_1^-$ and $A^-$, both of which form slightly soluble compounds with a reagent containing B-ions, we get a drop in $A_1^-$ very close to the point at which BA begins to precipitate. The magnitude of this drop is dependent upon the ratio between the solubility products $S_{BA_1}$ and $S_{BA}$, and upon the original ratio of the concentrations of $A_1^-$ and $A^-$.

If one of the ions is univalent and the other bivalent, the insoluble compounds have the formulas $BA_1$ and $B_2A$, $A^=$ being the bivalent anion. At the point where the solution is in equilibrium with both $BA_1$ and $B_2A$, we have:

$$[B^+] = \frac{S_{BA_1}}{[A_1^-]} = \sqrt{\frac{S_{B_2A}}{A^=}},$$

or,

$$\frac{[A_1^-]}{\sqrt{A^=}} = \frac{S_{BA_1}}{\sqrt{S_{B_2A}}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (32)$$

If $BA_1$ is the less soluble of the two salts, the addition of B-ions will precipitate $A_1^-$ alone as long as

$$\frac{[A_1^-]}{\sqrt{A^=}} > \frac{S_{BA_1}}{\sqrt{S_{B_2A}}}.$$

*Example.*—Let us consider a mixture of chloride and chromate which we are titrating with silver ion. Since $S_{AgCl}$ is about $10^{-10}$ and $S_{Ag_2CrO_4}$ about $10^{-12}$ we shall precipitate silver chloride alone until:

$$\frac{[Cl^-]}{\sqrt{[CrO_4^=}} = \frac{10^{-10}}{\sqrt{10^{-12}}} = 10^{-4},$$

or

$$[Cl^-] = 10^{-4}[CrO_4^=]^{0.5}.$$

When the chromate concentration is 0.1 normal, or rather $5 \times 10^{-2}$ molar, $\sqrt{[CrO_4^{=}]} = 2.25 \times 10^{-1}$, and the precipitation of silver chromate will not occur as long as:

$$[Cl^-] > 10^{-4} \times 2.25 \times 10^{-1} = 2.25 \times 10^{-5}.$$

From the above it is very easy to calculate, for more complicated cases, the conditions under which only one of the two ions will be precipitated, and also the point at which the precipitation of the second substance will begin.

**4. Influence of Acids upon the Solubility of Salts.**—The influence of acids upon the solubility of salts is a very important question. No detailed discussion of the subject will be given here, but stress will be laid on those facts which are of practical importance.

If the salt under consideration is the slightly soluble salt of a strong acid, strong acids will have about the same influence on its solubility as other strong electrolytes. According to Arrhenius' theory, or to the modern views of complete dissociation (Bjerrum, Debye), strong electrolytes increase the solubility of a salt. This influence, however, is so small compared with that which is to be discussed below that we may usually neglect it.

If, on the other hand, the salt in question is the slightly soluble salt of a weak acid, hydrogen ions will have an enormous influence on its solubility. In pure aqueous solutions we may assume that the salt BA is completely dissociated into its ions:

$$BA \rightleftarrows B^+ + A^-$$

(neglecting hydrolysis).

If the acid HA is weak, the A-ions will readily combine with hydrogen ions to form the undissociated acid:

$$H^+ + A^- \rightleftarrows HA.$$

Hence, when we add an acid to the suspension of BA the A-ions are removed to form undissociated acid, HA, and the solubility is increased to the limit set by the solubility product;

$$[B^+][A^-] = S_{BA} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we know the hydrogen-ion concentration, $S_{BA}$, and the dissociation constant of the acid HA, it is very easy to calculate the concentration of $B^+$, i.e., the solubility. As we shall see farther on, the dissociation constant, $K_{HA}$, is equal to:

$$K_{HA} = \frac{[H^+][A^-]}{[HA]}, \qquad (33)$$

and

$$[H^+] = K_{HA}\frac{[HA]}{[A^-]}. \qquad (34)$$

The total amount of BA that dissolves in the acid is equal to $[B^+]$, if we assume complete dissociation of strong electrolytes. It is also equal to the sum of the undissociated acid [HA] and $[A^-]$; hence:

$$[B^+] = [HA] + [A^-]. \qquad (35)$$

From equation (2) we have:

$$[B^+] = \frac{S_{BA}}{[A^-]}. \qquad (36)$$

Combining (35) and (36) we have:

$$[HA] = \frac{S_{BA}}{[A^-]} - [A^-], \qquad (37)$$

and from (34) and (37):

$$\frac{[H^+]}{K_{HA}} = \frac{S_{BA}}{[A^-]^2} - 1,$$

or

$$[A^-] = \sqrt{\frac{S_{BA}}{\frac{[H^+]}{K_{HA}} + 1}},$$

and

$$[B^+] = \sqrt{S_{BA}\left(\frac{[H^+]}{K_{HA}} + 1\right)}. \qquad (38)$$

At the point where $[H^+]$ is equal to the numerical value of $K_{HA}$ we obtain:

$$[B^+] = \sqrt{2S_{BA}} = 1.4S_{BA}.$$

In this particular instance the solubility has increased 1.4 times.

If the hydrogen-ion concentration is not known, but if we have added a given amount of a strong acid to a suspension of BA, we may derive another set of equations for the calculation of the solubility. In this case we make use of the general rule that the sum of cations is equal to the sum of anions. With the aid of the other equations we may find the relation between the different constants and the total concentration of the acid added. The above considerations are of importance for practical instances when we are dealing with slightly soluble salts of weak acids, in order to account for the influence of the hydrogen-ion concentration of the medium in which we are titrating upon the solubility of the salt. When we have a mixture of two anions, $A^-$ and $A_1^-$, both of which form insoluble salts with $B^+$, the one anion being derived from a strong and the other from a weak acid, we may prevent the precipitation of the salt of the latter by titrating in a strongly acid solution.

*Example.*—In neutral solution a mixture of chloride and phosphate gives a precipitate of silver chloride and phosphate with an excess of silver nitrate, whereas in acid solution only the silver chloride is precipitated.

**5. Formation of Slightly Dissociated Substances. Ionization of Water.**—Ions may combine with each other to form highly soluble though slightly dissociated compounds. Most compounds of the salt type are strong electrolytes; there are some mercuric salts, however, that are but slightly dissociated:

$$Hg^{++} + 2Cl^- \rightleftarrows HgCl_2.$$

The mercuric chloride is only dissociated to a very small extent.

The most important single reaction belonging to this group is that between hydrogen and hydroxyl ions, which unite to form very slightly dissociated water:

$$H^+ + OH^- \rightleftarrows H_2O. \quad . \quad . \quad . \quad . \quad . \quad (39)$$

This reaction governs the course of all neutralizations of acids and bases, and an extended discussion of it will therefore be given.[1] The mass-law relation derived from (39) is:

$$\frac{[H^+][OH^-]}{[H_2O]} = K, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (40)$$

which we may replace by the simpler expression:

$$[H^+][OH^-] = K_w, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (41)$$

because the molecular concentration of water may be regarded as constant in dilute solutions. $K_w$ is usually called the **dissociation constant** of water. This is not correct because the value of K in equation (40) is the dissociation constant of water. The authors prefer the name **ionization constant** (or ion product). The magnitude of the ionization constant of water depends to a great extent upon the temperature. It increases rapidly with rising temperature, as will be evident from the following table. $p_w$ represents the negative logarithm of the ionization constant, which will be called, throughout this book, the ionization exponent of water.

TABLE C

IONIZATION CONSTANT OF WATER AT DIFFERENT TEMPERATURES *

| Temperature | $K_w$ | $p_w$ |
|---|---|---|
| 0° | $0.12 \times 10^{-14}$ | 14.93 |
| 18° | $0.59 \times 10^{-14}$ | 14.23 |
| 25° | $1.04 \times 10^{-14}$ | 13.98 |
| 50° | $5.66 \times 10^{-14}$ | 13.25 |
| 100° | $58.2 \times 10^{-14}$ | 12.24 |

* Kohlrausch and Heydweiller, Ann. der Phys. (4), **28**, 512 (1909).

At room temperature, $K_w$ is approximately $10^{-14}$. Hence in pure water, where $[H^+] = [OH^-]$, we have at room temperature:

$$[H^+] = [OH^-] = \sqrt{K_w} = \sqrt{10^{-14}} = 10^{-7}. \quad . \quad . \qquad (42)$$

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[1] For special discussion of neutralization reactions, etc., *cf.* W. M. Clark, The Determination of Hydrogen Ions, 2d Ed., Baltimore, 1922; I. M. Kolthoff, The Use of Indicators (Farbenindikatoren) 2d Ed., an English translation which is to be published by John Wiley & Sons, is now in preparation (by N. H. Furman).

We may define as neutral reaction:

$$[H^+] = [OH^-] = 10^{-7} \quad \textbf{neutral reaction,}$$

and

$$[H^+] > 10^{-7} > [OH^-] \quad \textbf{acid reaction,}$$

$$[H^+] < 10^{-7} < [OH^-] \quad \textbf{alkaline reaction.}$$

It is usually preferable to express the values as ion exponents rather than to work with the ion concentrations. (*Cf.* § 1, p. 2.) $p_H$ represents the **hydrogen exponent**; $p_{OH}$ is the **hydroxyl exponent.**

We find from equation (41):

$$p_H + p_{OH} = p_w, \quad \ldots \ldots \quad (42)$$

where $p_w$ is the ionization exponent of water, with the value 14 at room temperature.

Then we have:

$$p_H = 14 - p_{OH}. \quad \ldots \ldots \quad (43)$$

$$p_{OH} = 14 - p_H. \quad \ldots \ldots \quad (44)$$

If $p_H$ is known we can calculate $p_{OH}$ directly, and conversely: We may define the reaction of a liquid in terms of ion exponents.

$$p_H = 7 = p_{OH} \quad \text{neutral reaction.}$$

$$p_H < 7 < p_{OH} \quad \text{acid reaction.}$$

$$p_H > 7 > p_{OH} \quad \text{alkaline reaction.}$$

*Illustration.*—In a 0.001 molar solution of hydrochloric acid $[H^+] = 10^{-3}$; hence $p_H = 3$. In this solution

$$p_{OH} = 14 - 3 = 11,$$

and $[OH^-] = 10^{-11}$. The reaction is acid. In a 0.001 molar solution of sodium hydroxide, $[OH^-] = 10^{-3}$, and $p_{OH} = 3$. In this solution $p_H = 14 - 3 = 11$ and $[H^+] = 10^{-11}$: alkaline reaction.

**6. Dissociation Constants of Acids and Bases.**—We may classify acids or bases as strong or weak electrolytes. Strong electrolytes are practically completely dissociated into ions. To this group belong, for example: the simple halogen acids, nitric acid, perchloric acid; the alkali and alkaline earth hydroxides, etc. Weak electrolytes are not completely dissociated. When we consider a weak acid we have:

$$HA \rightleftarrows H^+ + A^-, \quad \ldots\ldots \quad (45)$$

and

$$\frac{[H^+]\,[A^-]}{[HA]} = K_a. \quad \ldots\ldots \quad (46)$$

$K_a$ is the **dissociation constant** of the acid, and [HA] represents the concentration of the undissociated part. In a pure solution of the acid, $[H^+] = [A^-]$, and in such a solution:

$$[H^+] = \sqrt{K_a[HA]}. \quad \ldots\ldots \quad (47)$$

If the total acid concentration is $c$, then $[HA] = c - [H^+]$, and

$$[H^+] = \sqrt{K_a(c - [H^+])}. \quad \ldots\ldots \quad (48)$$

In many cases $[H^+]$ is very small in comparison with $c$; therefore we may often use, instead of (48), the simple equation:

$$[H^+] = \sqrt{K_a c}, \quad \ldots\ldots \quad (49)$$

and

$$p_H = \tfrac{1}{2}p_a - \tfrac{1}{2}\log c, \quad \ldots\ldots \quad (50)$$

$p_a$, which we will call the acid exponent, is the negative logarithm of $K_a$.

*Illustration.*—We wish to find $[H^+]$ and $p_H$ in a 0.1 molar acetic acid solution. $c = 0.1$; $K_a = 1.8 \times 10^{-5}$, or $p_a = 4.75$.

$$[H^+] = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3},$$

$$p_H = 2.375 + 0.5 = 2.875.$$

When $[H^+]$ is more than 5 per cent of $c$, it is not permissible to put the term $(c - [H^+])$ equal to $c$, and the more complicated equation (48) must be used. By rearranging this equation we obtain the following one, which is generally applicable:

$$[H^+] = -\frac{K_a}{2} + \sqrt{\frac{K_a{}^2}{4} + K_a c}\,^2. \quad \ldots \quad (51)$$

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[2] *Cf.* N. Schoorl, Rec. trav. chim., **40**, 616 (1921), for a graphical method of determining $p_H$ in these cases. See also, Kolthoff, Use of Indicators, 2d Ed., p. 8.

*Polybasic Acids.*—Acids that contain several replaceable hydrogen atoms dissociate step by step. Each step corresponds to the tendency of one of the hydrogen atoms to ionize, and possesses its own characteristic ionization constant, $K_1$, $K_2$, $K_3$, etc.

The first dissociation constant is always greater than the second, etc.

$$H_2A \rightleftarrows H^+ + HA^-. \qquad (52)$$

$$HA^- \rightleftarrows H^+ + A^=. \qquad (52a)$$

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]}. \qquad (53)$$

$$K_2 = \frac{[H^+][A^=]}{[HA^-]}. \qquad (54)$$

In most cases the first-step dissociation is so much greater than the second that we may neglect the latter in a pure solution of the acid. We can apply equation (53) for the calculation of $[H^+]$ in such a solution, just as we should do in the case of a monobasic acid. If the simplification is not permissible, by combining several equations [3] we may derive the exact equation:

$$[H^+]^3 - [H^+]^2K_1 - [H^+](K_1c - K_1K_2) = K_1K_2c. \qquad (55)$$

*Bases.*—Entirely similar relations apply to bases. If we represent the electrolytic dissociation of a base as:

$$BOH \rightleftarrows B^+ + OH^-,$$

we have:

$$\frac{[B^+][OH^-]}{[BOH]} = K_b. \qquad (56)$$

$K_b$ is the dissociation constant of the base.

**7. Hydrolysis of Salts.**—The temperature and the nature of the salt determine the degree of hydrolysis in the solution of a salt, BA. Both anion and cation can react with the ions of water:

$$B^+ + H_2O \rightleftarrows BOH + H^+. \qquad (57)$$

$$A^- + H_2O \rightleftarrows HA + OH^-. \qquad (58)$$

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[3] *Cf.* Kolthoff, The Use of Indicators, p. 9.

When we consider salts of strong acids and strong bases we find that both BOH and HA are completely dissociated. Hence their salts are not hydrolyzed to any appreciable extent and the salt does not change the reaction of the water. The hydrogen-ion concentration of these salt solutions lies close to $10^{-7}$, or $p_{\mathrm{H}} = 7$, at room temperature. Upon addition of excess of acid or base to such solutions the $p_{\mathrm{H}}$ is changed in the same way as that of pure water.

When the salt is made up of a strongly basic and a weakly acidic constituent, or *vice versa*, the relations are of general importance, and especially so for neutralizations. If, for example, we have a salt of a weak base and a strong acid, the reaction will occur according to equation (57) and the solution will have an acid reaction. On the other hand, the salt of a strong base and a weak acid will have an alkaline reaction.

When both constituents of the salt are weak, hydrolysis is very marked. The reactions are represented by (57) and (58). The reaction of these solutions will be nearly neutral, provided the difference between the dissociation constants of the acid and base is not too great. For our purposes a knowledge of the hydrogen-ion concentrations of hydrolyzed salt solutions is of great importance. We must be able to calculate the change in reaction upon the addition of a small excess of acid or base.

We shall first consider the hydrolysis of a salt of a weak base and a strong acid. The hydrolysis is represented by equation (57). When we apply the law of mass action we find:

$$\frac{[\mathrm{BOH}][\mathrm{H}^+]}{[\mathrm{B}^+]} = \mathrm{K}_{hyd}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

$\mathrm{K}_{hyd}$ is the hydrolysis constant. According to equation (41):

$$[\mathrm{H}^+] = \frac{\mathrm{K}_w}{[\mathrm{OH}^-]},$$

and from (56):

$$\frac{[\mathrm{B}^+][\mathrm{OH}^-]}{[\mathrm{BOH}]} = \mathrm{K}_b.$$

Upon combining these three equations we have:

$$K_{hyd} = \frac{K_w}{K_b} = \frac{[BOH][H^+]}{[B^+]}. \quad . \quad . \quad . \quad . \quad (60)$$

When the degree of hydrolysis is not too small we may neglect the $[OH^-]$ in comparison with $[H^+]$.[4] Then, in a pure salt solution:

$$[H^+] = [BOH].$$

Since the salt is a strong electrolyte, which is practically completely dissociated, $[B^+]$ is equal to the total salt concentration (if the hydrolyzed portion is negligible in comparison with the total salt concentration). Then the hydrogen-ion concentration in the solution of a salt of a weak base is:

$$[H^+] = \sqrt{\frac{K_w}{K_b}c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61)$$

$$p_H = 7 - \tfrac{1}{2}p_b - \tfrac{1}{2}\log c. \quad . \quad . \quad . \quad . \quad . \quad (62)$$

If the salt is one of a weak acid and a strong base, we find in the same way, for its solution:

$$[H^+] = \sqrt{\frac{K_w K_a}{c}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (63)$$

$$p_H = 7 + \tfrac{1}{2}p_a + \tfrac{1}{2}\log c. \quad . \quad . \quad . \quad . \quad (64)$$

*Illustration.*—Suppose we wish to calculate the hydrogen-ion concentration of a molar ammonium chloride solution. $c = 1$; $K_b = 1.8 \times 10^{-5}$, or $p_b = 4.75$. Hence:

$$p_H = 7 - 2.375 = 4.625, \quad \text{and} \quad [H^+] = 2.37 \times 10^{-5}.$$

*Influence of a small excess of acid or base on the hydrogen-ion concentration of the solution of the salt* BA.—In the discussion of neutralization curves we shall see that it is of importance to calculate the change in the hydrogen-ion concentration of a hydrolyzed salt solution when we add a very small excess of acid or base. Consider the salt of a strong acid and a weak base, the hydrolysis of which is represented by equation (57). If we add a small excess of a strong acid, i.e., hydrogen ions, then the hydrolysis will be repressed. Let us put the concentration of BOH and of $H^+$, formed by hydrolysis, equal to $x$. Now if the concentration of the acid added is $a$, the total $[H^+]$ of the solution is $(a + x)$, while [BOH] is equal to $x$.

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[4] *Cf.* N. Bjerrum, Die Theorie alkalimetrischen und azidimetrischen Titrierungen, Ahrens Sammlung, **21**, 12 (1915), or Stuttgart (1914).

If the total salt concentration is $c$, we have, according to equation (60):

$$\frac{(a + x)x}{c} = \frac{K_w}{K_b},$$

$$x = -\frac{a}{2} + \sqrt{\frac{a^2}{4} + c\frac{K_w}{K_b}}. \quad . \quad . \quad . \quad (65)$$

If, on the other hand, we add a small excess of BOH, equal to $b$, we obtain the same kind of equation for the calculation of $x$:

$$x = -\frac{b}{2} + \sqrt{\frac{b^2}{4} + c\frac{K_w}{K_b}}. \quad . \quad . \quad . \quad (66)$$

In a pure salt solution, $a$ and $b$ are equal to zero, and we have the customary hydrolysis equation.

*Example.*—To a 0.1 molar ammonium chloride solution we add hydrochloric acid corresponding to a concentration of $10^{-4}$ normal. Hence $a = 10^{-4}$; $c = 10^{-1}$; $K_b = 10^{-4.75}$. Then we find that $x = 5 \times 10^{-7}$. In this case the suppression of hydrolysis is so great that we may neglect $x$ in comparison with $a$. If, on the other hand, the original degree of hydrolysis is very marked, or if $a$ is very small, $x$ must be taken into account. If, in our instance of 0.1 molar ammonium chloride, $a$ is taken as $10^{-5}$, we find for $x = 4 \times 10^{-6}$, and

$$[H^+] = 10^{-5} + 0.4 \times 10^{-5} = 1.4 \times 10^{-5}.$$

If we are dealing with salts of the type $B_2A$, in which $A^=$ is the anion of the weak dibasic acid, $H_2A$, or with $BA_2$, where $B^{++}$ is the cation of a diacid base, all equations for hydrolysis remain the same. In this case we must use for $K_a$ the second dissociation constant of the acid, and for $K_b$ the second dissociation constant of the base.

*Salts of Weak Acids and Weak Bases.*—As stated above, the hydrolysis takes place according to equations (57) and (58). By combining the equations:

$$\frac{[BOH][H^+]}{[B^+]} = \frac{K_w}{K_b}. \qquad (60)$$

$$\frac{[HA][OH^-]}{[A^-]} = \frac{K_w}{K_a},$$

and

$$[H^+][OH^-] = K_w \ (41),$$

we have:

$$\frac{[BOH][HA]}{[B^+][A^-]} = \frac{K_w}{K_aK_b}. \qquad (67)$$

In most practical instances the value of $K_a$ lies between 100 and $\frac{1}{100}$ $K_b$. Under these conditions the hydrogen-ion concentration of the water is changed to such a small extent that we make no appreciable error in assuming that the amount of BOH that is formed by hydrolysis is equal to [HA]; [BOH] = [HA]. Since the salt of a weak acid and a weak base is a strong electrolyte, we may put $[B^+]$ and also $[A^-]$ equal to the total salt concentration, $c$ (neglecting that portion of the salt which is hydrolyzed). Then from equation (67):

$$\frac{[BOH]^2}{c^2} = \frac{[HA]^2}{c^2} = \frac{K_w}{K_aK_b}. \qquad (68)$$

$$[BOH] = [HA] = c\sqrt{\frac{K_w}{K_aK_b}}. \qquad (69)$$

By combining equations (60) and (69) we find that the hydrogen-ion concentration of the solution of a salt of a weak acid and a weak base is:

$$[H^+] = \sqrt{\frac{K_wK_a}{K_b}}. \qquad (70)$$

$$p_H = 7 + \tfrac{1}{2}p_a - \tfrac{1}{2}p_b. \qquad (71)$$

We have the remarkable result that the hydrogen-ion concentration is independent of the total salt concentration. Here again, it is necessary to emphasize the fact that all of the simple equations are valid only when $K_a$ lies between 100 and $\frac{1}{100}$ $K_b$, and the degree of hydrolysis is not more than 5 to 10 per cent. If the hydrolysis is greater we must correct $c$ for the hydrolyzed portion, and insert $c - [\mathrm{BOH}]$, or $c - [\mathrm{HA}]$, respectively, in place of $c$ in the equation.

*Examples.*—The simplest illustration is ammonium acetate. Here $K_a = K_b = 10^{-4.75}$; hence, from equation (71), we know that:

$$p_{\mathrm{H}} = 7 + 2.375 - 2.375 = 7.$$

In all salt solutions where $K_a$ is equal to $K_b$ we have an exactly neutral reaction.

A solution of ammonium formate has an acid reaction, for $K_a$ is greater than $K_b$. $K_a = 10^{-3.67}$, $K_b = 10^{-4.75}$, hence:

$$p_{\mathrm{H}} = 7 + 1.835 - 2.375 = 6.46.$$

*Change of the hydrogen-ion concentration in the solution of the salt of a weak acid and a weak base by addition of a small excess of acid or of base.*—In studying neutralization curves it is necessary to know the change of $[\mathrm{H}^+]$ in the neighborhood of the equivalence-point. If we add an excess of the acid HA corresponding to a concentration $a$, the total concentration of HA will be $a + x$, where $x$ is the concentration of the HA formed by hydrolysis. Then, according to our assumptions [BOH] will also be equal to $x$. According to equation (67) we have:

$$\frac{(a + x)x}{c^2} = \frac{K_w}{K_aK_b},$$

$$x = -\frac{a}{2} + \sqrt{\frac{a^2}{4} + c^2\frac{K_w}{K_aK_b}}. \quad . \quad . \quad . \quad (72)$$

If $x$ is known we may calculate $[\mathrm{H}^+]$:

$$[\mathrm{H}^+] = \frac{[\mathrm{HA}]}{[\mathrm{A}^-]}K_a = \frac{a + x}{c}K_a. \quad . \quad . \quad . \quad . \quad (73)$$

We obtain a similar equation for $x$ if we add an excess $b$ of the base BOH to the solution.

*Illustration.*—We wish to find the change in the hydrogen-ion concentration of a 0.1 molar ammonium acetate solution upon the addition of an excess of acetic acid corresponding to a concentration of $10^{-3}$ normal. $c = 10^{-1}$; $a = 10^{-3}$. $K_a = K_b = 10^{-4.75}$.

$$x = -5 \times 10^{-4} + \sqrt{25 \times 10^{-8} + 10^{-2}\frac{10^{-14}}{10^{-9.5}}} = 2.55 \times 10^{-4},$$

$$(a + x) = 1.25 \times 10^{-3},$$

$$[H^+] = \frac{1.25 \times 10^{-3}}{10^{-1}} \times 10^{-4.75} = 2.24 \times 10^{-7}.$$

$$p_H = 6.65.$$

If we had added an excess of ammonia corresponding to a concentration of $10^{-3}$, $p_H$ would become 7.35.

**8. The Reaction in a Mixture of a Weak Acid and Its Salt, or of a Weak Base and its Salt.**—When we add to the solution of a weak acid an excess of one of its salts, the degree of dissociation of the acid is diminished. From equation (46) we may calculate that:

$$[H^+] = \frac{[HA]}{[A^-]}K_a. \qquad (74)$$

In most practical cases, the dissociation of the acid is negligible in comparison with the excess of the salt that we add. We may therefore put [HA] equal to the total concentration $a$ of the acid, and $[A^-]$ equal to the concentration, $c$, of the salt added. Then we have:

$$[H^+] = \frac{a}{c}K_a. \qquad (75)$$

$$p_H = p_a - \log a + \log c. \qquad (76)$$

In the particular case in which $a$ is equal to $c$, we find that the hydrogen-ion concentration has the same numerical value as the dissociation constant.

When we are dealing with a base, we find:

$$[\mathrm{OH}^-] = \frac{b}{c}\mathrm{K}_b, \quad \ldots \ldots \ldots \quad (77)$$

or

$$[\mathrm{H}^+] = \frac{\mathrm{K}_w c}{\mathrm{K}_b b}. \quad \ldots \ldots \ldots \quad (78)$$

$$p_\mathrm{H} = p_w - p_b - \log c + \log b. \quad \ldots \quad (79)$$

In cases where the dissociation of the acid is still appreciable in the presence of an excess of the salt, the simple equations may not be applied. We have to take into consideration the dissociation represented by the equation:

$$\mathrm{HA} \rightleftarrows \mathrm{H}^+ + \mathrm{A}^-.$$

The dissociated acid gives equal amounts of $\mathrm{H}^+$ and $\mathrm{A}^-$. If we call this fraction $x$, then the concentration of the undissociated portion of the acid is $a - x$, and the total concentration of A-ions is $c + x$, whereas $[\mathrm{H}^+]$ equals $x$. According to equation (75) we have:

$$x = \frac{a - x}{c + x}\mathrm{K}_a. \quad \ldots \ldots \ldots \quad (80)$$

$$x = -\frac{c + \mathrm{K}_a}{2} + \sqrt{\left(\frac{a + \mathrm{K}_a}{2}\right)^2 + a\mathrm{K}_a} \quad \ldots \quad (81)$$

If we are titrating the salt of a weak acid with a strong acid, it is important to know how the reaction changes in the neighborhood of the point where all of the weak acid is liberated. For this reason a detailed discussion of the question has been given here.

**9. Mixtures of Two Weak Acids. Hydrolysis of Acid Salts.** —When we have a mixture of two weak acids of quite different dissociation constants, we must calculate how the hydrogen-ion concentration changes at the point where the amount of base that has been added is equivalent to the stronger acid. By studying these relations we can predict whether the titration of a given acid is possible in the presence of a weaker one.

Let us consider two acids, $H_1A_1$ and $H_2A_2$, with dissociation constants of $K_1$ and $K_2$, respectively. In a mixture of the acids, together with a definite amount of base, the hydrogen-ion concentration will be:

$$[H^+] = \frac{[H_1A_1]}{[A_1^-]}K_1 = \frac{[H_2A_2]}{[A_2^-]}K_2, \quad . \quad . \quad . \quad (82)$$

and

$$\frac{[H_1A_1]}{[A_1^-]} : \frac{[H_2A_2]}{[A_2^-]} = K_2 : K_1. \quad . \quad . \quad . \quad . \quad (83)$$

$\frac{[HA]}{[A^-]}$ is the reciprocal of the familiar " neutralization ratio " of an acid. We see from equation (83) that the neutralization ratio of the two acids is equal to the quotient of the dissociation constants. When there is a large difference between $K_1$ and $K_2$, the stronger acid, $H_1A_1$, alone will be neutralized at the beginning of the titration, while the amount of the second neutralized will be negligibly small. But, near the point where practically all of the stronger acid has been neutralized, there will also occur some neutralization of the second acid.

Let us assume that at the first equivalence-point, i.e., the point where an amount of base that is equivalent to the stronger acid has been added, *a* per cent of the stronger acid has been transformed to salt; then the second acid is neutralized to the extent of $(100 - a)$ per cent, if both $[H_1A_1]$ and $[H_2A_2]$ had the same original value. Hence $[H_1A_1]$ and $[H_2A_2]$ here represent the total concentrations of acid neutralized and not neutralized, respectively. Hence:

$$[A_1^-] = \frac{a}{100 - a}[H_1A_1],$$

and

$$[A_2^-] = \frac{100 - a}{a}[H_2A_2].$$

From equation (82) we have:

$$[H^+]^2 = \frac{[H_1A_1]}{[A_1^-]}K_1 \times \frac{[H_2A_2]}{[A_2^-]}K_2. \quad . \quad . \quad . \quad (84)$$

We may conclude from the foregoing that at the first equivalence-point:

$$[H^+]^2 = \frac{100 - a}{a} \times \frac{a}{100 - a} K_1K_2,$$

or

$$[H^+] = \sqrt{K_1K_2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (85)$$

$$p_H = \tfrac{1}{2}(p_{K_1} + p_{K_2}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (86)$$

When we are dealing with a mixture of two bases, we have at the first equivalence-point:

$$p_H = p_w - \tfrac{1}{2}(p_{K_1} + p_{K_2}). \quad . \quad . \quad . \quad . \quad (87)$$

An acid salt of the type BHA may be considered as a mixture of two acids of different strengths, in which the stronger acid has been neutralized. We may therefore calculate the hydrogen-ion concentration of such a salt solution by:

$$[H^+] = \sqrt{K_1K_2}, \quad . \quad (85)$$

where $K_1$ is the dissociation constant of the first acid and $K_2$ that of the second. For very accurate calculations a somewhat more complicated form of the equation is used, viz.:

$$[H^+] = \sqrt{\frac{K_1K_2c}{K_1 + c}}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

$K_1$ is usually so small in comparison with $c$ that it may be neglected, and we then have equation (85).

*Illustrations*: *Sodium Bicarbonate.*—$K_1 = 3 \times 10^{-7}$; $K_2 = 6 \times 10^{-11}$. A solution of sodium bicarbonate therefore has:

$$[H^+] = \sqrt{3 \times 10^{-7} \times 6 \times 10^{-11}} = 4.35 \times 10^{-9}; \; p_H = 8.37.$$

*Sodium Bitartrate*: $K_1 = 1 \times 10^{-3}$; $K_2 = 9 \times 10^{-5}$. In 0.1 molar solution we have:

$$[H^+] = \sqrt{1 \times 10^{-3} \times 9 \times 10^{-5}} = 3 \times 10^{-4}; \; p_H = 3.52.$$

We must use the more complicated equation (88) for more dilute solutions; for 0.001 molar solution we find:

$$[H^+] = 2.1 \times 10^{-4}; \quad p_H = 3.68.$$

In our consideration of the mixture of two acids, $H_1A_1$ and

$H_2A_2$, we assumed that both acids had the same concentration. If the original concentrations are different, equation (85) will be changed slightly. If, for example, the concentration of $H_1A_1$ is twice that of $H_2A_2$, we have:

$$[H^+] = \sqrt{\frac{K_1K_2}{2}}. \quad \dots \dots \quad (89)$$

$$p_H = \tfrac{1}{2}(p_{K_1} + p_{K_2}) + \tfrac{1}{2}\log 2 = \tfrac{1}{2}(p_{K_1} + p_{K_2}) + 0.15\,. \quad (90)$$

Hence $p_H$ is changed by only 0.15 at the first equivalence-point.

In general, if the ratio between the two acids is $r$ we get:

$$[H^+] = \sqrt{\frac{K_1K_2}{r}}, \quad \dots \dots \quad (91)$$

or

$$p_H = \tfrac{1}{2}(p_{K_1} + p_{K_2}) + \tfrac{1}{2}\log r. \quad \dots \quad (92)$$

**10. Change of Hydrogen-ion Concentration in a Mixture of Two Acids near the First Equivalence-Point.**—The accuracy of the titration of one acid in the presence of another depends upon the magnitude of the change in hydrogen-ion concentration near the first equivalence-point. We have seen, in the preceding paragraph, that a small amount of the first acid, $H_1A_1$, is not neutralized at the first equivalence-point. If this portion is $a$ per cent of the total concentration of $H_1A_1$, then $H_2A_2$ will be $a$ per cent neutralized if both acids had the same initial concentration. Now let us assume that we add 1 per cent of base in excess; most of this base will then be used for the neutralization of the second acid, $H_2A_2$, and only a small fraction will be used by $H_1A_1$, the concentration of which is already very small. If the part of the base that is used for the further neutralization of $H_1A_1$ is $x$ per cent of the total amount of $H_1A_1$, we have:

$$[A_1^-] = a + x,$$

$$[H_1A_1] = 100 - (a + x).$$

As there is an excess of 1 per cent of base, we find:

$$[A_2^-] = 100 - (a + x) + 1;$$

$$[H_2A_2] = a - x.$$

If we put these values in equation (83) we have:

$$\frac{100 - (a + x)}{(a + x)} \times \frac{101 - (a + x)}{(a - x)} = K_2 : K_1. \quad . \quad (93)$$

We thus obtain a quadratic equation which may be solved for $x$. If $x$ is known $[A_1^-]$ and $[H_1A_1]$ may be calculated, and hence $[H^+]$, from:

$$[H^+] = \frac{[H_1A_1]}{[A_1^-]}K_1.$$

*Examples.*—$K_1 : K_2 = 100$. At the first equivalence-point, $a = 91$; hence, $[H^+] = \frac{9}{91} K_1 = 0.099K_1$. Upon the addition of a 1 per cent excess of base, we find, from equation (93), $x = 0.4$, and we obtain $[H^+] = \frac{8.6}{91.4}K_1 = 0.094K_1$. Therefore in this case the hydrogen-ion concentration is only diminished by 5 per cent upon addition of 1 per cent excess of base, which corresponds to an increase of 0.02 in $p_H$.

When the ratio between $K_1$ and $K_2$ is much larger, the change in $p_H$ at the first equivalence-point increases.

$K_1 : K_2 = 10{,}000$. At the first equivalence-point, $a = 99$, and $[H^+] = \frac{1}{100} K_1$. By the addition of a 1 per cent excess of base we find $x = 0.38$, and hence $[H^+] = \frac{0.62}{100}K_1$; i.e., there is a change of 38 per cent in the hydrogen-ion concentration, corresponding to a $p_H$ variation of 0.21.

All of the foregoing equations are of value when we are dealing with a mixture of two bases. Instead of $[H^+]$ we always find $[OH^-]$, from which $[H^+]$ may be readily calculated.

**11. Formation of Complex Ions.**—The dissociation of a complex ion takes place in distinct steps. Let us assume that we have the simplest complex ion, $B_2A^+$. It is dissociated as follows:

$$B_2A^+ \rightleftarrows B^+ + BA. \quad . \quad . \quad . \quad . \quad . \quad . \quad (94)$$

$$BA \rightleftarrows B^+ + A^-. \quad . \quad . \quad . \quad . \quad . \quad . \quad (95)$$

Adding the two equations we have:

$$B_2A^+ \rightleftarrows 2B^+ + A^-. \quad . \quad . \quad . \quad . \quad . \quad . \quad (96)$$

By application of the law of mass action we find:

$$\frac{[B^+][BA]}{[B_2A^+]} = K_{\text{compl.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (97)$$

$K_{\text{compl.}}$ is the complex constant, or dissociation constant of the complex ion; BA is the neutral portion from which the complex is formed. $[B^+]$ is equal to $[BA]$ in a pure solution of the salt, if we may neglect the dissociation of BA into $B^+$ and $A^-$. Since complex salts are strong electrolytes we may put $[B_2A^+]$ equal to the total concentration $c$, if the dissociation of the complex ion is not too great. In such a solution we have:

$$[B^+] = \sqrt{K_{\text{compl.}}\, c}. \quad . \quad . \quad . \quad . \quad (98)$$

This is the same kind of expression that we found for the relation of $[H^+]$ and total concentration in a solution of a weak acid. (*Cf.* equation (49) p. 21.)

The change in $[B^+]$ upon the addition of an excess of a solution containing B-ions may be found by the method described in the discussion of the change in hydrogen-ion concentration of a solution of an acid upon the addition of an excess of one of the ions. If, for example, we add an excess of $[B^+]$ corresponding to $b$, then the total $[B^+]$ concentration will be $(b + x)$, while $[BA] = x$. Then

$$(b + x)x = K_{\text{compl.}}\, c,$$

and

$$x = -\frac{b}{2} + \sqrt{\frac{b^2}{4} + K_{\text{compl.}}\, c}. \quad . \quad . \quad . \quad (99)$$

When the neutral part, BA, of the complex ion is a strong electrolyte, which is usually the case, it is dissociated into its ions, and we must use equation (96) for the quantitative relations between the concentration of the complex ion and that of its constituent ions. According to (96):

$$\frac{[B^+]^2[A^-]}{[B_2A^+]} = K'_{\text{compl.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (97a)$$

When the neutral part, BA, is completely dissociated, we have in the pure solution of the complex ion:

$$[B^+] = 2[A^-],$$

and

$$[B^+]^3 = 2cK'_{\text{compl.}}$$

$$[B^+] = \sqrt[3]{2cK'_{\text{compl.}}} \quad . \quad . \quad . \quad . \quad . \qquad (98a)$$

$$[A^-] = \sqrt[3]{\frac{c}{4}K'_{\text{compl.}}}$$

The change in $[B^+]$ or $[A^-]$ that is caused by a small excess of one of these ions can be determined graphically by the method described for insoluble salts of the type $B_2A$ (see p. 10). The exact calculation involves a third-power equation which is difficult to solve.

*Illustration*:

$$Ag(CN)^-_2 \rightleftarrows Ag^+ + 2CN^-.$$

$$\frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = K'_{\text{compl.}} = 10^{-21.5}$$

Therefore we have, in an 0.1 molar solution containing only the complex silver cyanide:

$$[Ag^+] = \sqrt[3]{2.5 \times 10^{-23}} = 10^{-7.53} = 3.0 \times 10^{-8}.$$

$$[CN^-] = 2[Ag^+] = 6.0 \times 10^{-8}.$$

We often find cases where the neutral part, BA, is slightly soluble. This is the case, for example, with the complex silver cyanide ion, where AgCN is slightly soluble. If the solubility of BA is smaller than the value of its concentration in the pure solution of the complex salt, BA will precipitate before this point is reached. This is the case with mercuric iodide in the complex $HgI_4^=$. When the saturation point of BA is reached its concentration remains constant, and $[B^+]$ will vary according to the simple equation:

$$[B^+] = \frac{K_{\text{compl.}}}{S_{BA}}c = Kc; \quad . \quad . \quad . \quad . \quad . \quad . \qquad (100)$$

$S_{BA}$ represents the solubility product of BA.

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[5] This is the mean value of the data of Euler, Ber. **36**, 2878 (1903), and of Bodländer and Eberlein, Z. anorg. Chem., **39**, 208 (1924).

We see therefore that $[B^+]$ changes only with changes in the complex-ion concentration, $c$. Therefore, if precipitation of BA takes place before the complex ion is quantitatively formed, further addition of reagent scarcely affects the ion concentration. Hence we may only expect the titration to give satisfactory results when:

$$S_{BA} > \sqrt{K_{\text{compl.}}\,c}. \qquad \ldots\ldots \qquad (101)$$

i.e., when $S_{BA}$ is larger than the concentration of BA in the solution of the complex salt.

Thus far we have discussed only the dissociation of a simple complex, $B_2A^+$. If its composition is more complicated, all of the calculations become more involved:

$$B_3A^{++} \rightleftarrows 2B^+ + BA,$$

$$\frac{[B^+]^2[BA]}{[B_3A^{++}]} = K_{\text{compl.}} \qquad \ldots\ldots \qquad (102)$$

provided the dissociation of BA is negligible. In a pure solution of the complex ion we have:

$$[B^+]^3 = 2K_{\text{compl.}}\,c, \quad \text{or} \quad [B^+] = \sqrt[3]{2K_{\text{compl.}}\,c}. \quad . \quad (103)$$

If the neutral part is a strong electrolyte:

$$\frac{[B^+]^3[A^-]}{[B_3A^{++}]} = K'_{\text{compl.}} \qquad \ldots\ldots \qquad (102a)$$

and in a pure solution of the complex:

$$[B^+] = 3[A^-], \quad \text{or} \quad [B^+] = \sqrt[4]{3cK'_{\text{compl.}}} \quad . \quad . \quad (103a)$$

If it is desired to calculate the change in $[B^+]$ upon the addition of a small excess of B-ions, we may derive equations of the same kind as we did in the discussion of slightly soluble salts of the type $B_2A$, or $B_3A$. (*Cf.* p. 6.)

It is beyond the scope of this book to include a more detailed discussion of these matters. Anyone who has grasped the subject matter of this chapter should be able to derive, in any special case, a set of equations for the calculation of the change in ion concentrations upon addition of an excess of one component.

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Before discussing the equations that represent the course of oxidation-reduction reactions, it will be necessary to give a review of the relation between electron reactions and the potentials of electrodes.

# CHAPTER II

## ELECTRODE POTENTIALS. OXIDATION AND REDUCTION

**1. Potential of an Electrode.**—If a metal electrode is dipped into a solution of its ions, a difference of potential is developed between the metal and the solution. This potential difference is dependent in a special way upon the ion concentration of the solution, which is represented by the fundamental equation of Nernst (1889):

$$E = -\frac{RT}{nF} \ln \frac{P}{p}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (104)$$

where E is the potential difference, metal-solution; T the absolute temperature (273 + $t$ Centigrade); $n$ the valence of the ion; and F the Faraday, i.e., the quantity of electricity that is associated with 1 gram-equivalent, viz., 96,500 coulombs. R and F are constants, the values of which are known; moreover, we may transpose the natural logarithms to the Briggsian system (to the base 10) by dividing by 0.4343; we then have:

$$E = -\frac{0.0001983T}{n} \log \frac{P}{p}. \quad . \quad . \quad . \quad . \quad . \quad (105)$$

If the temperature is 18° C. we have:

$$E = -\frac{0.0577}{n} \log \frac{P}{p} \, (18° \text{ C.}), \quad . \quad . \quad . \quad (106)$$

or at 25° C.

$$E = -\frac{0.0591}{n} \log \frac{P}{p} \, (25° \text{ C.})^1. \quad . \quad . \quad (107)$$

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[1] For the sake of simplicity, a reference temperature of 25° C. will be used in the following discussion.

In these equations P is a constant for each metal; it is called the electrolytic solution pressure of the metal. $p$ is the osmotic pressure of those ions which the electrode is capable of supplying. In dilute solutions $p$ is proportional to the concentration $c$, and we obtain instead of equation (107):

$$E = -\frac{0.0591}{n} \log \frac{K}{c}, \quad . \; . \; . \; . \; . \; . \; . \quad (108)$$

or

$$E = -\frac{0.0591}{n} \log K + \frac{0.0591}{n} \log c. \quad . \quad (109)$$

If we dip the metal into a solution in which the concentration, $c$, of its ions is equal to 1, we have $\log c = 0$, and:

$$E = \frac{0.0591}{n} \log K. \; . \; . \; . \; . \; . \; . \; . \; . \quad (110)$$

This value of E in equation (110) is a constant for each metal, and depends only upon the temperature (and in special cases upon the concentration of the metal in the electrode). It is the so-called **electrolytic potential,** or **normal potential,** which is designated by the symbol $\epsilon_0$. Then we have:

$$E = \varepsilon_0 + \frac{0.0591}{n} \log c = \varepsilon_0 - \frac{0.0591}{n} p_I. \quad . \quad (111)$$

In this equation $p_I$ represents the ion exponent. The potential is a function of the ion concentration $c$, or $p_I$. When $c$ is increased ten times, or when $p_I$ becomes 1 unit smaller, the difference of potential between the electrode and the solution increases by $\frac{0.0591}{n}$ volt. When we are dealing with a univalent metal, $n$ is 1, and for each change of 1 in $p_I$ the potential changes 59.1 millivolts. With a bivalent ion, $n$ is 2, and the change of 1 in the ion exponent corresponds to only 29.5 millivolts.

If, instead of a metal, we have a non-metal electrode dipping into a solution of its ions, there is a potential difference which depends upon the ion concentration of the solution. If the concentration of the non-metal in the electrode is a constant, we may derive an equation of the same kind as the one derived for a metal electrode, viz.:

$$E_{\text{non-metal}} = \varepsilon_0 - \frac{0.0591}{n} \log c = \varepsilon_0 + \frac{0.0591}{n} p_{\text{I}}. \quad (112)$$

As we shall see later an unattackable metal electrode, such as platinum, or one of the other noble metals, when in contact with a non-metal, behaves like a non-metal electrode. The potential of a non-metal electrode changes in the same manner, but in the opposite direction to that of a metal electrode with changes in the ion concentration of the solution. Equation (111) shows that a metal electrode becomes more negative, i.e., less noble, with decreasing concentration of metal ion, whereas the metalloid electrode becomes more positive, i.e., more noble, with decreasing metalloid-ion concentration.

**2. Electron Reactions. Oxidation and Reduction.**—When a metal is in contact with a solution it has a tendency to send ions into the solution, as indicated by the equation:

$$M \rightleftarrows M^+ + e, \quad (113)$$

where $e$ represents the electron, or unit negative electric charge. Equation (113) is reversible; the metallic ions have a tendency to react with electrons to form electrically neutral metal atoms:

$$Ag \rightleftarrows Ag^+ + e,$$

$$Zn \rightleftarrows Zn^{++} + 2e.$$

The metal is more negative in proportion to its tendency to send ions into the solution; on the other hand, in proportion as more ions are discharged the metal is more noble. The tendency to send ions into the solution is governed by the electrolytic solution pressure, which was mentioned in the preceding section. When the metal supplies as many ions to the solution as are discharged from the latter to the electrode, it is exactly neutral. If more ions are sent into the solution than are discharged on the metal, the electrode has a negative charge. If more ions are discharged than are sent into the solution, the electrode receives a positive charge.

The same considerations apply to reactions at non-metallic electrodes. They may be expressed as follows:

$$Cl_2 + 2e \rightleftarrows 2Cl^-, \quad . \quad . \quad . \quad . \quad . \quad (114)$$

$$\tfrac{1}{2}O_2 + 2e \rightleftarrows 0^=.$$

Such an electrode will become more positive as more ions are discharged upon it, and conversely.

Since the reactions mentioned above are reversible, we may apply the law of mass action, and hence from equation (113):

$$\frac{[M^+][e]}{[M]} = K'.$$

The concentration of the discharged metal atoms may be regarded as constant, and we have:

$$[M^+][e] = S, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (115)$$

S being, according to the terminology of A. Smits and A. H. W. Aten,[2] the solubility product of the metal.

In similar manner we find for the reaction expressed in equation (114) the relation:

$$\frac{[Cl^-]^2}{[e]^2} = \phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (116)$$

$\phi$ being, according to Smits and Aten (*loc. cit.*), the solubility quotient of the non-metal. At present it is not possible to give the absolute values of S and $\phi$ as we do not know the concentration of *e*. We may calculate relative values which are referred to a standard in which we assume that $[e]$ is equal to one. Smits and Aten are doing so, basing their values on the lithium electrode as a standard. The authors suggest that possibly in the future, when more is known about the mechanism of complicated oxidation-reduction systems, the mode of expression that

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[2] A. Smits and A. H. W. Aten, Z. physik. Chem., **92**, 1 (1916).

Smits and Aten propose may be preferred for practical purposes to the usual electrochemical one. In the present state of our knowledge, there is still use for $[e]$, however.

In all cases where the valence of a substance is changed by the addition or withdrawal of electrons, we are dealing with reduction or oxidation. The addition of electrons results in the reduction of a substance, while their withdrawal results in oxidation.[3] Hence, when a metal is converted into its ions, we have an oxidation, because electrons are withdrawn. On the other hand, the transformation of a non-metal into its ions is reduction, as the non-metal unites with electrons.

As is well known, oxidation and reduction reactions play a very important rôle in nature. It is not necessary for one of the reacting substances to be discharged, as is the case with metals and non-metals. In general, every electron reaction promotes an oxidation or reduction; the two changes always occur simultaneously.

In a solution containing ferrous and ferric ions there may be a continuous exchange of electrons, as represented by the reversible equation:

$$\mathrm{Fe^{+++}} + e \rightleftarrows \mathrm{Fe^{++}},$$

or in similar fashion:

$$\mathrm{Sn^{++++}} + 2e \rightleftarrows \mathrm{Sn^{++}}.$$

Similar reactions may be written for anions:

$$\mathrm{Fe(CN)_6^{\equiv}} + e \rightleftarrows \mathrm{Fe(CN)_6^{----}}.$$

In accordance with the law of mass action, we have:

$$\frac{[\mathrm{Fe^{+++}}][e]}{[\mathrm{Fe^{++}}]} = \mathrm{K},$$

or, expressed in general form:

$$\frac{[\mathrm{Ox}][e]^n}{[\mathrm{Red}]} = \mathrm{K}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (117)$$

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[3] For a detailed discussion of the principles of oxidation and reduction, the reader is referred to W. Mansfield Clark, Public Health Reports reprint No. 823, p. 443 (1923).

In these simple oxidation-reduction reactions we have been dealing with isomerism of ions. There are also more complicated types of oxidation-reduction reactions in which the oxygen content of the ion is changed, e.g.:

$$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{++} + 2H_2O.$$

$$\frac{[MnO_2][H^+]^4[e]^2}{[Mn^{++}]} = K.$$

Here the equilibrium conditions are very largely dependent upon the hydrogen-ion concentration which enters to the fourth power in the above equation. The following are some other examples of very important reactions of this class:

$$MnO_4{}^-8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O,$$

$$Cr_2O_7{}^= + 14H^+6e \rightleftarrows 2Cr^{+++} + 7H_2O$$

In all of these reactions the hydrogen-ion concentration has an enormous influence on the equilibrium conditions:

$$\frac{[MnO_4{}^-][H^+]^8[e]^5}{[Mn^{++}]} = K.$$

**3. Oxidation-reduction Potentials.**[4]—"An evidence of some actual state of which [*e*] is representative is found in the fact that a noble metal placed in a solution containing an oxidation-reduction system acquires an electron charge increasing in intensity with increase in the reducing tendency . . ., i.e., the [*e*] value of the solution."[5] The noble metal containing free electrons is nothing else but an indicator of the [*e*] of the solution. Its potential is dependent upon the electron concentration in the solution and may be represented by the equation:

$$E = \frac{RT}{F} \ln \frac{A}{[e]}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (118)$$

A is a constant, therefore (118) becomes:

$$E = A' - 0.0591 \log [e]. \quad . \quad . \quad . \quad . \quad (119)^6$$

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[4] *Cf.* Text-books on electrochemistry; also W. M. Clark, *loc. cit.*

[5] Clark, *loc. cit.*

[6] The authors follow Clark (*loc. cit.*), closely in the formulation of equations (119)–(123).

From equation (117) we know that:

$$[e] = \sqrt[n]{\frac{[\mathrm{Red}]}{[\mathrm{Ox}]}}\mathrm{K}. \quad \ldots\ldots\ldots \quad (120)$$

Substituting this value of $[e]$ in (119), yields:

$$\mathrm{E} = \mathrm{A}' - \frac{0.0591}{n}\log\mathrm{K} - \frac{0.0591}{n}\log\frac{[\mathrm{Red}]}{[\mathrm{Ox}]}. \quad . \quad (121)$$

The term $\mathrm{A}' - \frac{0.0591}{n}\log\mathrm{K}$ is a constant for a given system. In case [Red] = [Ox] we have:

$$\mathrm{E} = \mathrm{A}' - \frac{0.0591}{n}\log\mathrm{K} = \varepsilon_0, \quad \ldots\ldots \quad (122)$$

$\varepsilon_0$ being the normal potential of the system. By combining (121) and (122) we obtain:

$$\mathrm{E} = \varepsilon_0 - \frac{0.0591}{n}\log\frac{[\mathrm{Red}]}{[\mathrm{Ox}]}. \quad \ldots\ldots\ldots \quad (123)$$

The equations applicable to metal or non-metal electrodes, given in § 1, are special forms of equation (123). For more complicated systems in which hydrogen ions play a rôle, we have:

$$\mathrm{E} = \varepsilon_0 - \frac{0.0591}{n}\log\frac{[\mathrm{Red}]}{[\mathrm{Ox}][\mathrm{H}^+]^m}, \quad \ldots\ldots \quad (124)$$

$n$ is the number of electrons; $m$ is the number of hydrogen ions that react with the oxidant. In the instance of the reduction of permanganate ion to manganous ion (*cf.* p. 43) $n$ is equal to 5, and $m$ to 8.

In the exact formulation of the potential in the more complicated oxidation-reduction systems, a difficulty arises from the fact that many of the reactions are not truly reversible. This is the case with the permanganate-manganous system and the dichromate-chromic system. In these cases equation (124) does not give correct results, and it is preferable to use empirical data for these special instances.

When we consider equation (123) we see that the oxidation-reduction potential is not dependent on the total concentration of oxidant and reductant, but merely upon the ratio $\frac{[\text{Red}]}{[\text{Ox}]}$. The value of $\varepsilon_0$ is a measure of the *intensity* of the tendency of the solution to oxidize or reduce, and not of its *capacity* to do so.

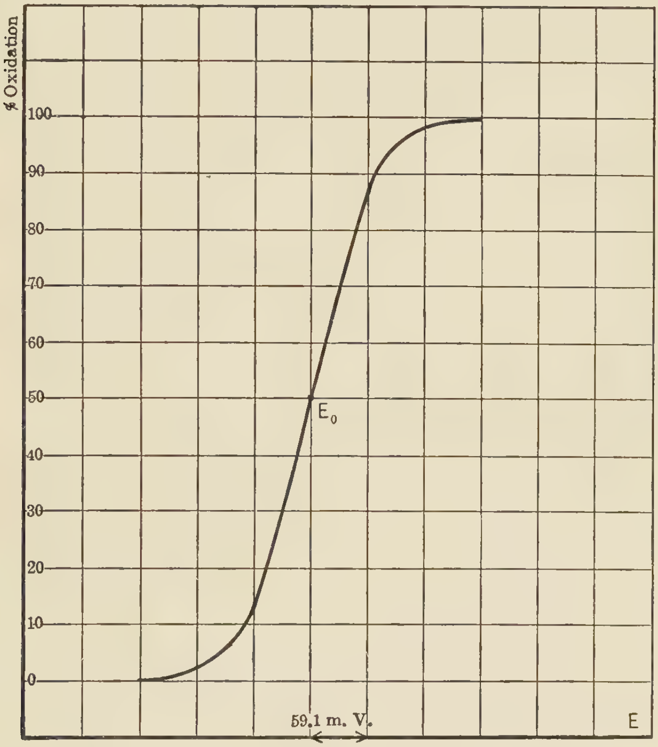

FIG. 3.—E.M.F. as a function of ratio [Ox] : [Red].

The latter is governed by the absolute amounts of oxidant or reductant, just as the **buffer capacity** of a buffer solution is governed by the absolute amounts of the components, and is not a measure of the real acidity, i.e., the $p_H$ of the solution. The potential of an oxidation-reduction electrode changes only with variations in the ratio $\frac{[\text{Red}]}{[\text{Ox}]}$ and not with the absolute amounts of the two. In instances where $n$ is equal to 1, the potential changes by 59.1 millivolts for a tenfold change in the ratio; when $n = 2$, the potential change is 29.5 millivolts.

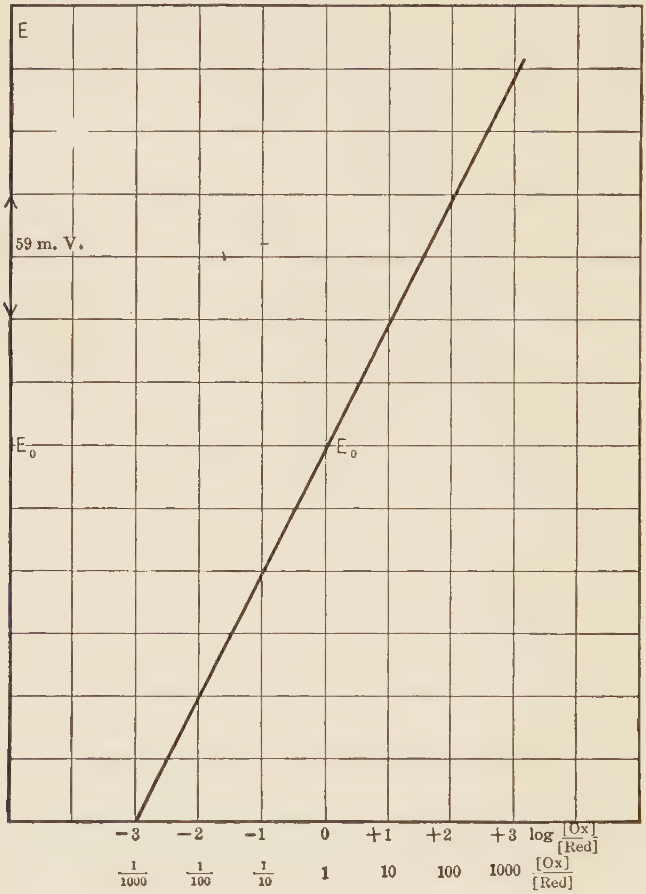

FIG. 4.—Logarithmic relation between E.M.F. and ratio $\frac{[Ox]}{[Red]}$.

If we plot the relation between the potential of an oxidation-reduction system and the ratio [Red] : [Ox] in a graph, we obtain the bilogarithmic curve that is plotted in Fig. 3. The ordinates give percentages of the substance in the oxidized form, while the abscissas are values of E in units of 59.1 millivolts each. When the solution is 50 per cent oxidized E has the value $\varepsilon_0$.

In Fig. 4 the logarithm of the ratio $\frac{[\text{Ox}]}{[\text{Red}]}$ has been plotted against the E.M.F. As we should expect from the equation, we get a straight line; for each change of 10 in the ratio, or of 1 in its logarithm, the E.M.F. changes by 59.1 millivolts at 25° C.

## CHAPTER III

## OXIDATION AND REDUCTION REACTIONS AND THEIR EQUILIBRIUM CONSTANTS

**1. Relation between the Normal Potentials and the Equilibrium Constant in an Oxidation-reduction Reaction.**—Let us consider the simple case of a piece of zinc dipped into a copper solution. The zinc has a tendency to give off ions to the solution:

$$\mathrm{Zn} \rightleftarrows \mathrm{Zn}^{++} + 2e,$$

whereas the copper ions have a tendency to be discharged:

$$\mathrm{Cu}^{++} + 2e \rightleftarrows \mathrm{Cu}.$$

Therefore we may expect the following reaction to take place to some extent:

$$\mathrm{Zn} + \mathrm{Cu}^{++} \rightleftarrows \mathrm{Zn}^{++} + \mathrm{Cu}. \quad . \quad . \quad . \quad . \quad (125)$$

As we have seen in the previous chapter, the equilibrium between zinc and zinc ions is represented by the Nernst equation:

$$E_{\mathrm{Zinc}} = \varepsilon_{0\mathrm{Zn}} + 0.029 \log [\mathrm{Zn}^{++}],$$

and similarly for copper:

$$E_{\mathrm{Copper}} = \varepsilon_{0\mathrm{Cu}} + 0.029 \log [\mathrm{Cu}^{++}].$$

The reaction represented by (125) will proceed until the potential of zinc is equal to that of copper. We shall then have a galvanic cell in which the potential of one electrode is the same as that of the other, and which therefore can no longer give a current. Hence when equilibrium is reached the conditions are such that $E_{\mathrm{Zinc}}$ is equal to $E_{\mathrm{Copper}}$ and we have:

$$\varepsilon_{0\mathrm{Zn}} + 0.029 \log [\mathrm{Z}^{++}] = \varepsilon_{0\mathrm{Cu}} + 0.029 \log [\mathrm{Cu}^{++}]. \quad (126)$$

$\varepsilon_{0\mathrm{Zn}} = -0.76$; $\varepsilon_{0\mathrm{Cu}} = +0.34$ (*Cf.* list at the end of this book, Table II)

From equation (126) we have:

$$0.76 + 0.34 = 0.029 \log \frac{[\mathrm{Zn}^{++}]}{[\mathrm{Cu}^{++}]};$$

and

$$\log \frac{[\mathrm{Zn}^{++}]}{[\mathrm{Cu}^{++}]} = \frac{1.1}{0.029} = 37.9.$$

Hence

$$\frac{[\mathrm{Zn}^{++}]}{[\mathrm{Cu}^{++}]} = 10^{37.9} = 8 \times 10^{38}.$$

It is evident that the equilibrium constant corresponding to (125)

$$\frac{[\mathrm{Zn}^{++}]}{[\mathrm{Cu}^{++}]} = \mathrm{K}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (127)$$

may be calculated from the normal potentials. There will be no equilibrium until the zinc-ion concentration is $8 \times 10^{38}$ times greater than the copper-ion concentration. Practically, this means that a piece of zinc will precipitate the copper completely from its solution. We may consider the reaction between one non-metal and the ions of another in the same way as we did that of the two metals.

$$2\mathrm{I}^- + \mathrm{Br}_2 \rightleftarrows \mathrm{I}_2 + 2\mathrm{Br}^-, \quad . \quad . \quad . \quad . \quad (128)$$

$$\frac{[\mathrm{Br}^-]^2}{[\mathrm{I}^-]^2} = \frac{[\mathrm{Br}^-]}{[\mathrm{I}^-]}\mathrm{K}. \quad . \quad . \quad . \quad . \quad . \quad (129)$$

For the sake of simplicity, it is assumed that the solution is saturated with respect to both halogens. As we have seen in the preceding chapter, the potential of a non-metallic electrode is represented by:

$$\mathrm{E} = \varepsilon_0 - \frac{0.059}{n} \log c. \quad . \quad . \quad (112)$$

For the reasons that have been discussed in connection with the reaction between a metal and the ions of another metal, the reaction represented in (128) will proceed until the potentials of both of the non-metallic electrodes are the same. When this point is reached, there is no further source of energy to drive the reaction in either direction. At equilibrium we have:

$$E_{I_2} = E_{Br_2} = \varepsilon_{0I_2} - 0.059 \log [I^-]$$
$$= \varepsilon_{0Br_2} - 0.059 \log [Br^-]. \quad . \quad . \quad (130)$$
$$\varepsilon_{0I_2} = + \ 0.54; \quad \varepsilon_{0Br_2} = + \ 1.08$$

(*Cf.* list at the back of this book, Table II).
Substituting these values in equation (113) we have:

$$1.08 - 0.54 = 0.54 = 0.059 \log \frac{[Br^-]}{[I^-]},$$
$$\log \frac{[Br^-]}{[I^-]} = \frac{0.54}{0.059} = 9.15,$$
$$\frac{[Br^-]}{[I^-]} = 10^{9.15} = 1.4 \times 10^9.$$

At the equilibrium-point the bromide-ion concentration in round numbers is $10^9$ times larger than the iodide concentration, if the solution is saturated with respect to both halogens.

We shall now consider, from a quite general viewpoint, the simple oxidation-reduction reaction:

$$Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2, \quad . \quad . \quad . \quad (131)$$

in which an oxidant,[1] $Ox_1$, reacts with a reducing agent, $Red_2$, to yield the reduced form of $Ox_1$, namely $Red_1$, and $Ox_2$, the oxidized form of the reductant. Then:

$$\frac{[Ox_1][Red_2]}{[Red_1][Ox_2]} = K. \quad . \quad . \quad . \quad . \quad . \quad . \quad (132)$$

As we have seen (p. 43), the following equation is valid for every oxidation-reduction system:

$$E = A' - 0.0591 \log [e], \quad . \quad . \quad . \quad . \quad . \quad (119)$$

when there is only one electron involved in the reaction; and

$$E = \varepsilon_0 + 0.0591 \log \frac{[Ox]}{[Red]}. \quad . \quad . \quad . \quad . \quad (123)$$

---

[1] The authors use the terms " oxidant " and " reductant " instead of the longer terms " oxidizing agent " and " reducing agent," respectively.

When equilibrium prevails, the potentials of both oxidation-reduction systems are the same, and we have:

$$\varepsilon_{0_1} + 0.0591 \log \frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} = \varepsilon_{0_2} + 0.0591 \log \frac{[\mathrm{Ox}_2]}{[\mathrm{Red}_2]}. \quad (133)$$

or:

$$\log \frac{[\mathrm{Ox}_1][\mathrm{Red}_2]}{[\mathrm{Red}_1][\mathrm{Ox}_2]} = \log \mathrm{K} = \frac{(\varepsilon_{0_2} - \varepsilon_{0_1})}{0.0591}, \quad (134)$$

and, in general, when $n$ electrons are involved:

$$\log \mathrm{K} = \frac{(\varepsilon_{0_2} - \varepsilon_{0_1})n}{0.0591}. \quad (135)$$

*Examples.*—We wish to find the equilibrium constant of the reaction:

$$\mathrm{Fe^{+++} + Cu^{+} \rightleftarrows Fe^{++} + Cu^{++}},$$

$$\frac{[\mathrm{Fe^{+++}}][\mathrm{Cu^{+}}]}{[\mathrm{Fe^{++}}][\mathrm{Cu^{++}}]} = \mathrm{K}.$$

Now

$$\varepsilon_{0\,\mathrm{Cu^{II}} \rightarrow \mathrm{Cu}} = +0.18; \quad \varepsilon_{0\,\mathrm{Fe^{III}} \rightarrow \mathrm{Fe^{II}}} = +0.714.$$

Application of equation (134) yields:

$$-\log \mathrm{K} = p_{\mathrm{K}} = \frac{0.534}{0.0591} = 9.05,$$

$$\mathrm{K} = 10^{-9.05} = 9 \times 10^{-10}.$$

Another reaction constant, which is of practical importance, is that for the reaction:

$$\mathrm{2Fe^{+++} + 2I^{-} \rightleftarrows 2Fe^{++} + I_2},$$

$$\frac{[\mathrm{Fe^{+++}}][\mathrm{I^{-}}]}{[\mathrm{Fe^{++}}]\sqrt{[\mathrm{I_2}]}} = \mathrm{K}.$$

$$\varepsilon_{0\,\mathrm{Fe^{III}} \rightarrow \mathrm{Fe^{II}}} = +0.714; \quad \varepsilon_{0\,\mathrm{I_2} \rightarrow 2\mathrm{I^-}} = +0.631,$$

$$-\log \mathrm{K} = p_{\mathrm{K}} = \frac{0.083}{0.0591} = 1.4.$$

$$\mathrm{K} = 4 \times 10^{-2}.$$

Changes in which the oxidant and reductant react with the loss or gain of the same number of electrons have been discussed (equation (131)ff.).

The relations are more complicated if the oxidant is reduced according to the equation:

$$\mathrm{Ox_1} + 2e \rightleftarrows \mathrm{Red_1},$$

whereas the reductant is oxidized thus:

$$\mathrm{Red_2} \rightleftarrows \mathrm{Ox_2} + e.$$

The reaction between $\mathrm{Ox_1}$ and $\mathrm{Red_2}$ is then expressed by the equation:

$$\mathrm{Ox_1} + 2\ \mathrm{Red_2} \rightleftarrows \mathrm{Red_1} + 2\ \mathrm{Ox_2}, \quad . \quad . \quad . \quad (136)$$

whence:

$$\frac{[\mathrm{Ox_1}][\mathrm{Red_2}]^2}{[\mathrm{Red_1}][\mathrm{Ox_2}]^2} = \mathrm{K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (137)$$

For the $\mathrm{Ox_1}$-$\mathrm{Red_1}$ system we have the equation:

$$\mathrm{E_1} = \varepsilon_{0_1} + \frac{0.0591}{2} \log \frac{[\mathrm{Ox_1}]}{[\mathrm{Red_1}]}.$$

And for the $\mathrm{Ox_2}$-$\mathrm{Red_2}$ system:

$$\mathrm{E_2} = \varepsilon_{0_2} + \frac{0.0591}{1} \log \frac{[\mathrm{Ox_2}]}{[\mathrm{Red_2}]}.$$

At equilibrium we have, according to equation (136):

$$\mathrm{E_1} = \mathrm{E_2},$$

or

$$\varepsilon_{0_1} + \frac{0.0591}{2} \log \frac{[\mathrm{Ox_1}]}{[\mathrm{Red_1}]} = \varepsilon_{0_2} + 0.0591 \log \frac{[\mathrm{Ox_2}]}{[\mathrm{Red_2}]}$$

$$= \varepsilon_{0_2} + \frac{0.0591}{2} \log \frac{[\mathrm{Ox_2}]^2}{[\mathrm{Red_2}]^2}. \quad (138)$$

$$\log \frac{[\mathrm{Ox_1}]}{[\mathrm{Red_1}]} \cdot \frac{[\mathrm{Red_2}]^2}{[\mathrm{Ox_2}]^2} = \log \mathrm{K} = \frac{2(\varepsilon_{0_2} - \varepsilon_{0_1})}{0.0591}. \quad . \quad (139)$$

In the same way we may derive an equation for the reaction:

$$\mathrm{Ox_1} + 3\ \mathrm{Red_2} \rightleftarrows \mathrm{Red_1} + 3\ \mathrm{Ox_2}:$$

$$\mathrm{K} = \frac{[\mathrm{Ox_1}]}{[\mathrm{Red_1}]} \frac{[\mathrm{Red_2}]^3}{[\mathrm{Ox_2}]^3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (140)$$

$$\log \mathrm{K} = \frac{3(\varepsilon_{0_2} - \varepsilon_{0_1})}{0.0591}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (141)$$

*Example.*—Let us derive the equilibrium constant for the reaction:

$$Sn^{++} + 2Fe^{+++} \rightleftarrows Sn^{++++} + 2Fe^{++}$$

$$\frac{[Sn^{++}]}{[Sn^{++++}]}\,\frac{[Fe^{+++}]^2}{[Fe^{++}]^2} = K.$$

In 1 N hydrochloric acid,

$$\varepsilon_{0\,Sn^{++++}\rightarrow Sn^{++}} = +0.138,$$

whereas

$$\varepsilon_{0\,Fe^{+++}\rightarrow Fe^{++}} = +0.714.$$

$$-\log K = \frac{2(0.714 - 0.138)}{0.0591} = 19.5$$

$$K = 10^{-19.5} = 3 \times 10^{-20}.$$

Having discussed a number of special instances, we shall now derive the general expression for the constant K of the general reaction:

$$a\ Ox_1 + b\ Red_2 \rightleftarrows a'\ Red_1 + b'\ Ox_2;$$

$$\frac{[Ox_1]^a}{[Red_1]^{a'}}\cdot\frac{[Red_2]^b}{[Ox_2]^{b'}} = K. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (142)$$

The characteristic electromotive force expressions for each oxidation-reduction system are:

$$E_1 = \varepsilon_{0a} + \frac{0.0591}{x}\log\frac{[Ox_1]^a}{[Red_1]^{a'}},$$

and

$$E_2 = \varepsilon_{0b} + \frac{0.0591}{x}\log\frac{[Ox_2]^b}{[Red_2]^{b'}}.$$

When equilibrium is established, $E_1 = E_2$, and we have:

$$\varepsilon_{0a} + \frac{0.0591}{x}\log\frac{[Ox_1]^a}{[Red_1]^{a'}} = \varepsilon_{0b} + \frac{0.0591}{x}\log\frac{[Ox_2]^b}{[Red_2]^{b'}}.$$

Whence:

$$\log\frac{[Ox_1]^a}{[Red_1]^{a'}}\cdot\frac{[Red_2]^{b'}}{[Ox_2]^b} = \log K = \frac{(\varepsilon_{0b} - \varepsilon_{0a})x}{0.0591}. \quad . \qquad (143)$$

Equation (143) is generally applicable; by means of it we may always calculate the equilibrium constants when the normal potentials are known.

It is of interest to note here that these considerations are also very important in ordinary analytical titrations. Most of these analytical processes have been developed in an empirical way. We are able to calculate, with the aid of the equilibrium constants (see Table II, p. 325), how far a given reaction will proceed toward completion.

*Examples.*—1. In the reaction:

$$Fe^{+++} + Cu^{+} \rightleftarrows Fe^{++} + Cu^{++},$$

which has been discussed above, $x$ is equal to 1, and

$$\log K = \frac{(\varepsilon_{0b} - \varepsilon_{0a})}{0.0591},$$

as found above in a different way.

2. When we apply equation (143) to the reaction:

$$2Fe^{+++} + Sn^{++} \rightleftarrows 2Fe^{++} + Sn^{++++},$$

we have the two partial systems:

$$Sn^{++++} + 2e \rightleftarrows Sn^{++}: \qquad E_1 = \varepsilon_{0\mathrm{SN}} + \frac{0.0591}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]}$$

$$2Fe^{+++} + 2e \rightleftarrows 2Fe^{++}: \qquad E_2 = \varepsilon_{0\mathrm{FE}} + \frac{0.0591}{2} \log \frac{[Fe^{+++}]^2}{[Fe^{++}]^2}.$$

In this case: $x = 2$; $a = a' = 1$; $b = b' = 2$; and

$$-\log K = \frac{(\varepsilon_{0\mathrm{FE}} - \varepsilon_{0\mathrm{SN}})2.}{0.0591}$$

3. The reaction between ferrous iron and potassium permanganate in acid solution may be represented by the equation:

$$MnO_4^{-} + 8H^{+} + 5Fe^{++} \rightleftarrows Mn^{++} + 5Fe^{+++} + 4H_2O;$$

$$\frac{[MnO_4^{-}][H^{+}]^8[Fe^{++}]^5}{[Mn^{++}][Fe^{+++}]^5} = K.$$

We have here the following oxidation-reduction systems:

$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O$:

$$E_1 = \varepsilon_{0_{MnO_4}} + \frac{0.0591}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{++}]},$$

$5Fe^{+++} + 5e \rightleftarrows 5Fe^{++}$:

$$E_2 = \varepsilon_{0_{Fe}} + \frac{0.0591}{5} \log \frac{[Fe^{+++}]^5}{[Fe^{++}]^5},$$

and $x = 5; \quad b = b' = 5; \quad a = a' = 1.$

$$-\log K = \frac{(\varepsilon_{0_{MnO_4}} - \varepsilon_{0_{Fe}})5}{0.0591}.$$

The $\varepsilon_0$ value of the permanganate is very largely dependent upon the hydrogen-ion concentration of the solution. When the latter is equal to 1 N, we have $\varepsilon_{0_{MnO_4}} = 1.52$, and since $\varepsilon_{0_{Fe}} = 0.71$, we have:

$$-\log K = \frac{(1.52 - 0.71)5}{0.0591} = 68.6,$$

and

$$K = 2.5 \times 10^{-69}.$$

**2. The Relation between the Concentrations at the Equivalence-point.**—As we have seen in the preceding section, we may consider an oxidation-reduction reaction to be reversible, and we may therefore apply the law of mass action to such a system. If the normal potential corresponding to each partial reaction is known we can calculate the equilibrium constant of the total reaction.

Consider the titration of a solution of an oxidizing agent: When we have added an equivalent amount of reductant, we have reached the equivalence-point, as we shall call it, i.e., the theoretical end-point of the titration. It is important, for several reasons, to know the relations between oxidant and reductant at the equivalence-point. Before the more general equations are introduced, let us consider the simple reaction:

$$Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2, \quad . \; . \; . \quad (131)$$

whose equilibrium constant:

$$K = \frac{[Ox_1]}{[Red_1]} \cdot \frac{[Red_2]}{[Ox_2]}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (132)$$

may be calculated, as we have seen in the preceding section. At the equivalence-point, when we have added an amount of reductant that is equivalent to the oxidant, we have:

$$[Ox_1] + [Red_1] = [Ox_2] + [Red_2].$$

Moreover, equivalent amounts of $Red_1$ and $Ox_2$ are formed, therefore:

$$[Red_1] = [Ox_2], \quad . \quad . \quad . \quad . \quad . \quad . \quad (144)$$

and

$$[Ox_1] = [Red_2]. \quad . \quad . \quad . \quad . \quad . \quad . \quad (145)$$

From (144), (145) and (132) we find at the equivalence-point:

$$K = \frac{[Ox_1]^2}{[Red_1]^2} = \frac{[Red_2]^2}{[Ox_2]^2},$$

or

$$\frac{[Ox_1]}{[Red_1]} = \frac{[Red_2]}{[Ox_2]} = \sqrt{K}. \quad . \quad . \quad . \quad (146)$$

From the above, we see that at the equivalence-point the ratio between the original oxidant and its reduction product, or between the original reductant and its oxidation product, *is independent of the total concentrations of these substances.*

*Example.*—For the reaction: $Fe^{+++} + Cu^{+} \rightleftarrows Fe^{++} + Cu^{+}$ we have seen that $-\log K = 9.05$ (*cf.* p. 51).

From equation (146) we find at the equivalence-point:

$$\frac{[Fe^{+++}]}{[Fe^{++}]} = \frac{[Cu^{+}]}{[Cu^{++}]} = 10^{-\frac{9.05}{2}} = 3.0 \times 10^{-5}.$$

We shall now consider the reaction:

$$Ox_1 + 2\,Red_2 \rightleftarrows Red_1 + 2\,Ox_2, \quad . \quad . \quad . \quad (136)$$

$$K = \frac{[Ox_1]\,[Red_2]^2}{[Red_1]\,[Ox_2]^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (137)$$

At the equivalence-point we have:

$$2\,[\mathrm{Ox}_1] + 2\,[\mathrm{Red}_1] = [\mathrm{Ox}_2] + [\mathrm{Red}_2],$$

and also:

$$2\,[\mathrm{Red}_1] = [\mathrm{Ox}_2], \quad \ldots\ldots \quad (147)$$

and

$$2\,[\mathrm{Ox}_1] = [\mathrm{Red}_2]. \quad \ldots\ldots \quad (148)$$

From (137), (147) and (148) we find at the equivalence-point:

$$\mathrm{K} = \frac{[\mathrm{Ox}_1]^3}{[\mathrm{Red}_1]^3} = \frac{[\mathrm{Red}_2]^3}{[\mathrm{Ox}_2]^3},$$

$$\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} = \frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]} = \sqrt[3]{\mathrm{K}}. \quad \ldots \quad (149)$$

The ratios are again independent of the total concentration of the solution to be titrated.

*Example.*—For the reaction:

$$\mathrm{Sn}^{++} + 2\mathrm{Fe}^{+++} \rightleftarrows \mathrm{Sn}^{++++} + 2\mathrm{Fe}^{++}$$

we have calculated that $-\log \mathrm{K} = 19.5$ (*cf.* p. 53).

From equation (149) we see that at the equivalence-point:

$$\frac{[\mathrm{Fe}^{+++}]}{[\mathrm{Fe}^{++}]} = \frac{[\mathrm{Sn}^{++}]}{[\mathrm{Sn}^{++++}]} = 10^{-\frac{19.5}{3}} = 3.2 \times 10^{-7}.$$

In the same way as we have done above, we may derive the conditions for the general case:

$$a\,\mathrm{Ox}_1 + b\,\mathrm{Red}_2 \rightleftarrows a'\,\mathrm{Red}_1 + b'\,\mathrm{Ox}_2,$$

$$\mathrm{K} = \frac{[\mathrm{Ox}_1]^a}{[\mathrm{Red}_1]^{a'}} \cdot \frac{[\mathrm{Red}_2]^b}{[\mathrm{Ox}_2]^{b'}}. \quad \ldots\ldots \quad (142)$$

At the equivalence-point, $a$ moles of $\mathrm{Ox}_1$ have reacted with $b$ moles of $\mathrm{Red}_2$. Hence, the ratio of the molecules that have not yet reacted must also be as $a : b$, or

$$\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_2]} = \frac{a}{b}. \quad \ldots\ldots \quad (150)$$

We see also that for $a'$ moles of $\mathrm{Red}_1$ formed there have been formed $b'$ moles of $\mathrm{Ox}_2$; hence, at the equivalence-point:

$$\frac{[\mathrm{Red}_1]}{[\mathrm{Ox}_2]} = \frac{a'}{b'}. \quad \ldots\ldots \quad (151)$$

From (150) and (151) it follows that:
$b\,[\mathrm{Ox}_1] = a\,[\mathrm{Red}_2]$, and $b'\,[\mathrm{Red}_1] = a'\,[\mathrm{Ox}_2]$,

or

$$\frac{b\,[\mathrm{Ox}_1]}{b'\,[\mathrm{Red}_1]} = \frac{a\,[\mathrm{Red}_2]}{a'\,[\mathrm{Ox}_2]};$$

$$\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} = \frac{ab'}{a'b}\,\frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]}. \quad . \quad . \quad . \quad . \quad . \quad (152)$$

$$\frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]} = \frac{a'b}{ab'}\,\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]}. \quad . \quad . \quad . \quad . \quad . \quad (153)$$

Therefore, at the equivalence-point we have:

$$\frac{a'b}{ab'}\,\frac{[\mathrm{Ox}_1]^{a+1}}{[\mathrm{Red}_1]^{a'+1}} = \frac{ab'}{a'b}\,\frac{[\mathrm{Red}_2]^{b+1}}{[\mathrm{Ox}_2]^{b'+1}} = \mathrm{K},$$

$$\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} = \sqrt[a+b]{\left(\frac{ab'}{a'b}\right)^{b}\mathrm{K}}. \quad . \quad . \quad . \quad . \quad (154)$$

$$\frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]} = \sqrt[a+b]{\left(\frac{a'b}{ab'}\right)^{a}\mathrm{K}}. \quad . \quad . \quad . \quad . \quad (155)$$

In practice, these complicated equations are simplified by the fact that there is usually a simple relation between $a$, $a'$ and $b$, $b'$. When $a = a'$, and $b = b'$, we have instead of (154) and (155) the simple equation:

$$\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} = \frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]} = \sqrt[a+b]{\mathrm{K}}. \quad . \quad . \quad . \quad . \quad (156)$$

$$(a = a' \quad \text{and} \quad b = b')$$

*Examples.*—In the reaction between ferric and cuprous ions the ratio at the equivalence-point is $\sqrt{\mathrm{K}}$.

In the reaction between ferric iron and stannous tin:

$$a = a' = 1; \quad b = b' = 2,$$

and the ratio at the equivalence-point is $\sqrt[3]{\mathrm{K}}$.

Now consider the reaction:

$$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5\mathrm{Fe^{++}} \rightleftarrows \mathrm{Mn^{++}} + 5\mathrm{Fe^{+++}} + 4\mathrm{H_2O},$$

for which we have calculated that $-\log K = 68.6$ at a hydrogen-ion concentration of 1 N. In this case, $a = a' = 1$; $b = b' = 5$, and at the equivalence-point we have:

$$\frac{[MnO_4^-]}{[Mn^{++}]} = \frac{[Fe^{++}]}{[Fe^{+++}]} = \sqrt[6]{K} = 10^{-\frac{68.6}{6}} = 10^{-11.4} = 4 \times 10^{-12}.$$

This calculation shows how far toward completion the reaction between permanganate and ferrous iron proceeds in acid solution.

**3. Change in Ratio between Oxidant and Reductant, and in their Concentrations, in the Neighborhood of the Equivalence-point.**—The potential of an oxidation-reduction electrode is not dependent upon the total concentrations of oxidant and reductant, but merely on the ratio of the two. Therefore, it is of interest for potentiometric purposes to find how the ratio between $[Ox_1]$ and $[Red_1]$, or between $[Red_2]$ and $[Ox_2]$, changes in the neighborhood of the equivalence-point. On the other hand, it is of interest for ordinary titrations to know the actual ion concentrations in connection with the sensitivity of the indicator and the accuracy of the titration.

We shall again consider first the simple reaction:

$$Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2. \quad . \quad . \quad . \quad . \quad (131)$$

$$\frac{[Ox_1][Red_2]}{[Red_2][Ox_2]} = K. \quad . \quad . \quad . \quad . \quad . \quad (132)$$

At the equivalence-point we have:

$$\frac{[Ox_1]}{[Red_1]} = \frac{[Red_2]}{[Ox_2]} = \sqrt{K}. \quad . \quad . \quad . \quad . \quad (146)$$

The sum of $[Ox_1]$ and $[Red_1]$ is known, and is, let us say, equal to $c$.

$$[Ox_1] + [Red_1] = [Ox_2] + [Red_2] = c. \quad . \quad . \quad (157)$$

Then at the equivalence-point we have:

$$[Red_1] = [Ox_2] = \frac{c}{1 + \sqrt{K}}. \quad . \quad . \quad (158)$$

$$[Ox_1] = [Red_2] = \frac{c\sqrt{K}}{1 + \sqrt{K}}. \quad . \quad . \quad (159)$$

We know that the titration of an oxidant or reductant, as represented in equation (131), gives good results only when the reaction goes practically completely to the right, or in other words when the equilibrium constant, K, is very small. In these cases $\sqrt{K}$ is negligible as compared with 1, and we have, instead of equations (158) and (159):

$$[Red_1] = [Ox_2] = c. \quad \ldots\ldots \quad (160)$$

$$[Ox_1] = [Red_2] = c\sqrt{K}. \quad \ldots \quad (161)$$

$c$ being the total concentration of each system.

Now let us assume that we add an excess of $Ox_1$ equal to $a$ (with an excess of $Red_2$ we should obtain the same equations). Then the total concentration of $Ox_1$ will be smaller than $a + c\sqrt{K}$, because the amount of $Ox_1$ and $Red_2$ at the equivalence-point is diminished, owing to incompleteness of the reaction, by an excess of one of the components on the left side of the equation. If we designate as $x$ the concentration of the $Ox_1$ and $Red_1$ that have not reacted in the presence of excess of one of the components, then the total concentration of $Ox_1$ will be $a + x$, and $[Red_2] = x$. Moreover, we may assume that the concentrations of $Red_1$ and $Ox_2$, which are already large at the equivalence-point in comparison with those of $[Ox_1]$ and $[Red_2]$, remain unchanged, i.e.:

$$[Red_1] = [Ox_2] = c.$$

By the application of equation (132) we find:

$$\frac{a + x}{c} \cdot \frac{x}{c} = K,$$

$$x = -\frac{a}{2} + \sqrt{\frac{a^2}{4} + Kc^2}. \quad \ldots \quad (162)$$

When $x$ becomes so small that it is negligible in comparison with the excess $a$, we have the simplified equation:

$$x = \frac{c^2}{a}K. \quad \ldots\ldots\ldots \quad (163)$$

In the presence of an excess $a$ of $Ox_1$ we have the ratio:

$$\frac{[Ox_1]}{[Red_1]} = \frac{-\frac{a}{2} + \sqrt{\frac{a^2}{4} + Kc^2}}{c}, \quad . \quad . \quad . \quad (164)$$

or whenever we may apply the simple equation (163):

$$\frac{[Ox]_1}{[Red_1]} = \frac{a}{c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (165)$$

In the same way we find for:

$$\frac{[Ox_2]}{[Red_2]} = \frac{c}{-\frac{a}{2} + \sqrt{\frac{a^2}{4} + Kc^2}}, \quad . \quad . \quad . \quad (166)$$

or when the simple equation (163) is applicable:

$$\frac{[Ox_2]}{[Red_2]} = \frac{a}{cK}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (167)$$

*Example.*—$Fe^{+++} + Cu^{+} \rightleftarrows Fe^{++} + Cu^{++}$. As was shown on p. 51, the equilibrium constant, K, for this reaction is $10^{-9.05}$. At the equivalence-point:

$$\frac{[Fe^{++}]}{[Fe^{+++}]} = \frac{[Cu^{+}]}{[Cu^{++}]} = \sqrt{10^{-9.05}} = 3.0 \times 10^{-5}.$$

Now let us assume that the total iron or copper concentration is 0.1 molar at the end-point. Then $c = 0.1$. If we add a 1 per cent excess of ferric ion, $a = 10^{-3}$, then $x = 1 \times 10^{-8}$, which may be considered negligible in comparison with $a$, and we may apply the simplified equations (165) and (167): Upon the addition of a 1 per cent excess of ferric ion, we find that the ratio $\frac{[Fe^{+++}]}{[Fe^{++}]}$ changes from $3 \times 10^{-5}$ to $10^{-2}$, and the ratio $\frac{[Cu^{+}]}{[Cu^{++}]}$ from $3 \times 10^{-5}$ to $9 \times 10^{-8}$.

If $c$ were not 0.1 molar, but had any other value, we should find the same variations in the ratio upon adding 1 per cent excess of ferric ion. *Hence the change of the ratio* $\frac{[Ox_1]}{[Red_1]}$ or $\frac{[Red_2]}{[Ox_2]}$ *is independent of the total concentration of oxidant or reductant to be titrated.*

We have for the reaction:

$$\mathrm{Ox_1} + 2\,\mathrm{Red_2} \rightleftarrows \mathrm{Red_1} + 2\,\mathrm{Ox_2}. \quad . \quad . \quad . \qquad (136)$$

$$\frac{[\mathrm{Ox_1}]}{[\mathrm{Red_1}]}\,\frac{[\mathrm{Red_2}]^2}{[\mathrm{Ox_2}]^2} = \mathrm{K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (137)$$

And we know that at the equivalence-point:

$$\frac{[\mathrm{Ox_1}]}{[\mathrm{Red_1}]} = \frac{[\mathrm{Ox_2}]}{[\mathrm{Red_2}]} = \sqrt[3]{\mathrm{K}}, \quad . \quad . \qquad (149)$$

and $[\mathrm{Red_2}] + [\mathrm{Ox_2}] = c$, whereas $[\mathrm{Ox_1}] + [\mathrm{Red_1}] = \frac{1}{2}c$, where $\frac{1}{2}c$ is the sum of the molar concentrations of the oxidant and its reduction product at the equivalence-point. If the reaction is practically complete at the equivalence-point, we may again assume, as in the preceding case, that:

$[\mathrm{Red_1}] = \frac{1}{2}c$, and $[\mathrm{Ox_2}] = c$. If now $[\mathrm{Ox_1}] = \frac{1}{2}x$, and $[\mathrm{Red_2}] = x$, we have from equation (137):

$$\frac{\frac{1}{2}x^3}{\frac{1}{2}c^3} = \mathrm{K}, \quad \text{or} \quad x = c\sqrt[3]{\mathrm{K}}. \quad . \quad . \quad . \quad . \qquad (168)$$

If we add a small excess of $\mathrm{Red_2}$ we may assume that $[\mathrm{Red_1}]$ and $[\mathrm{Ox_2}]$ remain unchanged. This is entirely permissible in practical cases. Then it is possible to derive a new set of equations, from which the total concentration of $[\mathrm{Red_2}] = a + x$ and $[\mathrm{Ox_1}] = \frac{1}{2}x$ may be found. These equations are complicated, however, (third-power equations). Therefore we shall assume the simpler case where $x$ is negligible in comparison with $a$. Then we have:

$$[\mathrm{Red_2}] = a; \quad \text{also} \quad [\mathrm{Red_1}] = \tfrac{1}{2}c, \quad \text{and} \quad [\mathrm{Ox_2}] = c;$$

and:

$$\frac{[\mathrm{Ox_1}]a^2}{\frac{1}{2}cc^2} = \mathrm{K}, \quad \text{or} \quad [\mathrm{Ox_1}] = \frac{c^3}{2a^2}\mathrm{K}. \quad . \quad . \qquad (169)$$

If we add an excess $a$ of $\mathrm{Ox_1}$ we find:

$$[\mathrm{Red_2}] = \sqrt{\frac{c^3}{2a}\mathrm{K}}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (170)$$

If the value of $[\mathrm{Ox_1}]$ in equation (169) or of $[\mathrm{Red_2}]$ in equation (170) is not negligible in comparison with $a$, it is advisable to plot the values of $[\mathrm{Ox_1}]$ or $[\mathrm{Red_2}]$ against $a$ in a graph, and to derive the correction values from this graph. (*Cf.* Solubility products, p. 9.) Having the expressions for $[\mathrm{Ox}_1]$ or $[\mathrm{Red}_2]$ in the presence of an excess of one of the components, we may calculate the change of the ratio $\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]}$, or of $\frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]}$, under these conditions. In the presence of an *excess a of Red*$_2$, we find:

$$\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} = \frac{c^2}{a^2}\mathrm{K}, \tag{171}$$

and

$$\frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]} = \frac{a}{c}. \tag{172}$$

In the presence of an *excess a of Ox*$_1$, however, we have:

$$\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} = \frac{2a}{c}. \tag{173}$$

$$\frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]} = \frac{c}{2a}\mathrm{K}. \tag{174}$$

If we express $a$ in per cent of $c$ we find again that the change in the ratios which we desire to determine is independent of the total concentration.

*Example*: $\mathrm{Sn}^{++} + 2\mathrm{Fe}^{+++} \rightleftarrows \mathrm{Sn}^{++++} + 2\mathrm{Fe}^{+++}$,

$$\frac{[\mathrm{Sn}^{++}][\mathrm{Fe}^{+++}]^2}{[\mathrm{Sn}^{++++}][\mathrm{Fe}^{++}]^2} = 10^{-19.5} = 3 \times 10^{-20}.$$

At the equivalence-point:

$$\frac{[\mathrm{Fe}^{+++}]}{[\mathrm{Fe}^{++}]} = \frac{[\mathrm{Sn}^{++}]}{[\mathrm{Sn}^{++++}]} = 10^{-6.5} = 3.2 \times 10^{-7}.$$

If the sum of the concentrations of ferrous and ferric iron is equal to $c$, and if we have a 1 per cent excess of ferric iron, then $\frac{c}{a} = 10^{-2}$, and $\frac{c}{a} = 100$. In the presence of this excess we have:

$$\frac{[\mathrm{Fe}^{+++}]}{[\mathrm{Fe}^{++}]} = \frac{c}{a} = 10^{-2}, \tag{172}$$

and

$$\frac{[\mathrm{Sn}^{++}]}{[\mathrm{Sn}^{++++}]} = \frac{c^2}{a^2}\mathrm{K} = 10^{-15.5} = 3.2 \times 10^{-16}. \tag{171}$$

Both values were equal to $3.2 \times 10^{-7}$ at the equivalence-point; hence the $\frac{[Fe^{+++}]}{[Fe^{++}]}$ has increased $3 \times 10^4$ times, whereas $\frac{[Sn^{++}]}{[Sn^{++++}]}$ has decreased $10^9$ times. In the presence of 0.1 per cent ferric iron, the ratios would be:

$$\frac{[Fe^{+++}]}{[Fe^{++}]} = \frac{a}{c} = 10^{-3} \quad (\text{an increase of } 3 \times 10^3 \text{ times})$$

$$\frac{[Sn^{++}]}{[Sn^{++++}]} = 10^{-13.5} \quad (\text{a decrease of } 10^7 \text{ times}).$$

If we add an excess of 1 per cent of stannous tin (referred to the concentration of the stannic form) we find:

$$\frac{2a}{c} = 10^{-2}, \quad \text{and} \quad \frac{c}{2a} = 10^2.$$

In the presence of this excess we have:

$$\frac{[Fe^{+++}]}{[Fe^{++}]} = \sqrt{100K} = \sqrt{10^{-17.5}} = 10^{-8.75} = 1.8 \times 10^{-9},$$

and

$$\frac{[Sn^{++}]}{[Sn^{++++}]} = 10^{-2}.$$

The ratio $\frac{[Fe^{+++}]}{[Fe^{++}]}$ has been decreased 180 times with 1 per cent excess of stannous tin, whereas it is increased 30,000 times by a 1 per cent excess of ferric iron. From this we see that the changes in the ratios between oxidant and reductant are not symmetrical on both sides of the equivalence-point.

We shall now consider the more general case:

$$a \, Ox_1 + b \, Red_2 \rightleftarrows a' \, Red_1 + b' \, Ox_2.$$

For the sake of simplicity the discussion will be limited to those instances in which there are formed from $Ox_1$ an equal number of molecules of $Red_1$, and from $Red_2$ an equal number of molecules of $Ox_2$; hence:

$$a = a', \quad \text{and} \quad b = b'.$$

Then we have:

$$\left(\frac{[Ox_1]}{[Red_1]}\right)^a\left(\frac{[Red_2]}{[Ox_2]}\right)^b = K. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (142)$$

At the equivalence-point:

$$\frac{[Ox_1]}{[Red_1]} = \frac{[Red_2]}{[Ox_2]} = \sqrt[a+b]{K}. \quad . \quad . \quad (156)$$

If, at the equivalence-point: $[Ox_1] + [Red_1] = c$, we have $[Red_2] + [Ox_2] = \frac{b}{a}c$. If the reaction is practically complete at the equivalence-point, then:

$$[Red_1] = c; \quad [Ox_2] = \frac{b}{a}c.$$

If $[Ox_1] = x$, then $[Red_2] = \frac{b}{a}x$. From these relations and equation (156) we find at the equivalence-point:

$$[Ox_1] = x = c\sqrt[a+b]{K}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (175)$$

$$[Red_2] = \frac{b}{a}x = \frac{b}{a}c\sqrt[a+b]{K}. \quad . \quad . \quad . \quad . \quad . \quad (176)$$

We assume once more that $[Red_1]$ and $[Ox_2]$ remain unchanged upon the addition of an excess $\alpha$ of $Ox_1$. If we put the excess of $Ox_1$ equal to the total concentration of $Ox_1$, we have:

$$[Ox_1] = \alpha; \quad [Red_2] = x; \quad [Red_1] = c, \quad \text{and} \quad [Ox_2] = \frac{b}{a}c.$$

From these relations, and from equation (156), it follows that:

$$\left(\frac{\alpha}{c}\right)^a \frac{[Red_2]^b}{\left(\frac{b}{a}c\right)^b} = K. \quad [Red_2] = \frac{b}{a}c\sqrt[b]{\left(\frac{c}{\alpha}\right)^a K}.$$

Then in the presence of an excess $\alpha$ of $Ox_1$, we have:

$$\frac{[Ox_1]}{[Red_1]} = \frac{\alpha}{c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (177)$$

$$\frac{[Red_2]}{[Ox_2]} = \sqrt[b]{\left(\frac{c}{\alpha}\right)^a K}. \quad . \quad . \quad . \quad . \quad . \quad (178)$$

In the presence of an excess $\beta$ of $\text{Red}_2$, we have $[\text{Red}_2] = \beta$; $[\text{Ox}_2] = \frac{b}{a}c$; $[\text{Red}_1] = c$, and

$$\frac{[\text{Ox}_1]^a}{c^a}\left(\frac{\beta}{\frac{b}{a}c}\right)^b = \text{K};$$

$$[\text{Ox}_1] = c\sqrt[a]{\left(\frac{\frac{b}{a}c}{\beta}\right)^b \text{K}}.$$

In the presence of an excess $\beta$ of $\text{Red}_2$ we then have:

$$\frac{[\text{Ox}_1]}{[\text{Red}_1]} = \sqrt[a]{\left(\frac{\frac{b}{a}c}{\beta}\right)^b \text{K}}. \quad . \quad . \quad . \quad . \qquad (179)$$

$$\frac{[\text{Red}_2]}{[\text{Ox}_2]} = \frac{\beta}{\frac{b}{a}c}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (180)$$

From equations (177) to (180) we see that the change in the ratios between oxidant and reductant in the neighborhood of the equivalence-point is independent of the total concentrations of the substances present, provided we express the amounts of the excesses added as fractions of these total concentrations.

*Example.*—We shall again consider the reaction:

$$\text{MnO}_4{}^- + 8\text{H}^+ + 5\text{Fe}^{+++} \rightleftarrows \text{Mn}^{++} + 5\text{Fe}^{+++} + 4\text{H}_2\text{O}.$$

If the hydrogen-ion concentration remains constant at 1 N, we have:

$$\frac{[\text{MnO}_4{}^-][\text{H}^+]^8[\text{Fe}^{++}]^5}{[\text{Mn}^{++}][\text{Fe}^{+++}]^5} = \text{K} = 10^{-68.6} = 2.5 \times 10^{-69} \ (\textit{cf.} \text{ p. } 55).$$

In this instance $a = 1$, and $b = 5$. At the equivalence-point we have:

$$\frac{[\text{MnO}_4{}^-]}{[\text{Mn}^{++}]} = \frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]} = \sqrt[1+5]{10^{-68.6}}$$

$$= 10^{-11.43} = 3.7 \times 10^{-12}. \quad . \quad . \qquad (156)$$

If the total concentration at the equivalence-point is 0.1 molar, then $[\text{Fe}^{+++}] = 0.1$, and $[\text{Mn}^{++}] = c = \frac{1}{5} \times 0.1$ and

$$[\text{Fe}^{++}] = 0.1\sqrt[6]{10^{-68.6}} = 3.7 \times 10^{-13}. \quad . \quad (176)$$

$$[\text{MnO}_4^{-}] = 0.02\sqrt[6]{10^{-68.6}} = 0.74 \times 10^{-13}. \quad . \quad (174)$$

Now if we add an excess of 0.1 per cent of ferrous iron, we find:

$$\frac{\beta}{\frac{b-c}{a}} = 10^{-3}, \quad \text{and} \quad \frac{\frac{b-c}{a}}{\beta} = 10^{3}.$$

In the presence of a 0.1 per cent excess of ferrous iron we have:

$$\frac{[\text{MnO}_4^{-}]}{[\text{Mn}^{++}]} = (10^{3})^{5}10^{-68.6} = 10^{-53.6} = 2.5 \times 10^{-54} \quad (179)$$

$$\frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]} = 10^{-3}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (180)$$

The ratio $\frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]}$ has been changed from $3.7 \times 10^{-12}$ at the equivalence-point to $10^{-3}$ by this excess of ferrous iron, and the ratio $\frac{[\text{MnO}_4^{-}]}{[\text{Mn}^{++}]}$ has decreased $7 \times 10^{41}$ times. The changes that are made by the addition of 0.1 per cent excess of permanganate are quite different: $\frac{\alpha}{c} = 10^{-3}$

$$\frac{c}{\alpha} = 10^{3}.$$

In the presence of this excess of permanganate we have:

$$\frac{[\text{MnO}_4^{-}]}{[\text{Mn}^{++}]} = 10^{-3}. \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (181)$$

$$\frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]} = \sqrt[5]{10^{3}\text{K}} = 10^{-12.72} = 1.9 \times 10^{-13} \quad . \quad (182)$$

Hence the ratio $\frac{[\text{Fe}^{++}]}{[\text{Fe}^{+++}]}$ has been decreased only 20 times by addition of 0.1 per cent excess of permanganate, whereas the increase of this ratio by an addition of 0.1 per cent of ferrous iron is $3 \times 10^8$ times.

**4. Change in Ratio between an Oxidant and its Reduction Product upon Precipitation of One of the Components.**—When we have a mixture of an oxidizing agent and its reduction product and add a solution that gives a precipitate with one of the components, the concentration of the other component decreases a little, owing to the increasing dilution. If we neglect the change in volume, we may say that one of the concentrations remains unchanged whereas the other disappears because of the precipitation. We have here the combination of a precipitation reaction with an oxidation-reduction system.

Let us assume, for example, that we have a mixture of ferri- and ferrocyanide, and that we are titrating the latter with a lead solution. The ferricyanide does not react, and its concentration $c$ in the neighborhood of the equivalence-point remains constant. The ferrocyanide concentration, however, is decreased by the precipitation:

$$\mathrm{Fe(CN)}_6^{\equiv} + 2\mathrm{Pb}^{++} \rightleftarrows \mathrm{Pb_2Fe(CN)_6}.$$

The manner in which the ion concentrations change in the neighborhood of the equivalence-point was discussed in Chapter I. If we call the concentrations of the ferrocyanide $x$, $x'$, $x''$, etc., respectively, we have the corresponding ratios:

$$\frac{[\mathrm{Feoc}]}{[\mathrm{Feic}]}\,[2] = \frac{x}{c} \quad \text{or} \quad \frac{x'}{c}, \frac{x''}{c} \ldots \text{etc.}$$

from which we see that the ratio changes in proportion to the variation of the ferrocyanide concentration. In Part Two we shall see that we may make several important applications of reactions of this kind (determination of zinc, lead, etc.; the use of the iodine electrode, etc.).

**5. Determination of One Reductant or Oxidant in the Presence of a Second.**—When we have two different reducing

[2] Following the usage of Erich Müller, the authors write the expression Feoc for ferrocyanide ion, and Feic for ferricyanide.

agents of quite different reduction intensities (reduction potentials) in a solution, it is possible to oxidize one, more or less quantitatively, before the other is oxidized. If we have, for example, a solution of stannous and ferrous ions which we are titrating with a strong oxidant, such as permanganate, the stannous tin is oxidized first, after which the ferrous iron is oxidized to the ferric state.

The discussion of this special case can be shown to follow from the general cases that have been discussed in this chapter. At the first equivalence-point where all of the stannous ion is oxidized, we have the equilibrium:

$$\mathrm{Sn^{++} + 2Fe^{+++} \rightleftarrows Sn^{++++} + 2Fe^{++}}.$$

As explained on p. 51, if we know the normal potential of each system we may calculate the equilibrium constant of the reaction; and from the latter, we may deduce the changes in the ratios $\frac{[\mathrm{Sn^{++}}]}{[\mathrm{Sn^{++++}}]}$ and $\frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}]}$ in the neighborhood of the equivalence-point.

In general, we may say that when we are titrating a mixture of two reductants, $\mathrm{Red_1}$ and $\mathrm{Red_2}$, with a strong oxidizing agent, at the first equivalence-point where the amount of oxidant that is added is equivalent to $\mathrm{Red_1}$, we are dealing with the reaction:

$$a\,\mathrm{Red_1} + b\,\mathrm{Ox_2} \rightleftarrows a'\,\mathrm{Ox_1} + b'\,\mathrm{Red_2}.$$

All that has been said about this reaction in the preceding paragraphs may be applied here.

These considerations are also valid when we are titrating a mixture of two oxidants with a strong reductant. As we shall see in Part Two, simple separate determinations, which are of great practical importance, may be made in this way.

# CHAPTER IV

# RELATION BETWEEN THE CHANGE OF THE ION CONCENTRATIONS AND ELECTRODE POTENTIAL IN COMBINATIONS OF IONS

**1. Potential at the Equivalence-point in Precipitation Reactions. Equivalence-point Potential (Equivalence-potential).**—When we have added an equivalent amount of precipitating reagent to the solution of an ion we have reached the **equivalence-point,** or the **theoretical end-point,** of the titration. *This is not the same as the actual end-point, for the latter includes the titration error.* For this reason the authors prefer the name "equivalence-point" rather than "end-point."

The electrode whose potential indicates the change in concentration of the ion to be titrated is called the **indicator electrode.** In the present work, the potential at the equivalence-point will be called the **equivalence-point potential, $E_E$,**[1] or simply, the **equivalence-potential.**

If we consider the general reaction:

$$xB^{n+} + yA^{m-} \rightleftarrows B_xA_y,$$

we have, according to equations (25*a*) to (29*a*), at the equivalence-point:

$$[B^{n+}] = \sqrt[x+y]{\left(\frac{x}{y}\right)^y S_{B_xA_y}}. \quad . \quad . \quad . \quad . \quad . \quad (25a)$$

$$[A^{m-}] = \sqrt[x+y]{\left(\frac{y}{x}\right)^x S_{B_xA_y}}. \quad . \quad . \quad . \quad . \quad . \quad (26a)$$

$$p_B = \frac{1}{x+y}\left(p_S - y\log\frac{x}{y}\right). \quad . \quad . \quad (28a)$$

$$p_A = \frac{1}{x+y}\left(p_S - x\log\frac{y}{x}\right). \quad . \quad . \quad (29a)$$

---

[1] Erich Müller, "Die Elektrometrische Massanalyse," Dresden (1923), p. 22, uses the name "Umschlagspotential" (inflection-potential). For the theoretical reasons mentioned above, the authors prefer the term equivalence-potential.

From the above and from equation (111), we find that the equivalence-potential $E_{EB}$ of electrode B will be:

$$E_{EB} = \varepsilon_{0B} + \frac{0.0591}{n(x+y)}\left(\log S_{B_xA_y} + y\log\frac{x}{y}\right)$$

$$= \varepsilon_{0B} - \frac{0.0591}{n(x+y)}\left(p_S - y\log\frac{x}{y}\right), \quad . \quad . \quad . \quad (183)$$

and

$$E_{EA} = \varepsilon_{0A} - \frac{0.0591}{m(x+y)}\left(\log S_{B_xA_y} + x\log\frac{y}{x}\right)$$

$$= \varepsilon_{0A} + \frac{0.0591}{m(x+y)}\left(p_S + x\log\frac{x}{y}\right). \quad . \quad . \quad . \quad (184)$$

*Examples.*—If $B^+$ and $A^-$ are univalent, as is the case with the silver halides, then at the equivalence-point:

$$E_{EB} = \varepsilon_{0B} - \frac{0.0591}{2}p_S.$$

$$E_{EA} = \varepsilon_{0A} + \frac{0.0591}{2}p_S.$$

If $B^+$ is univalent, and A bivalent, as in the case of silver chromate, silver oxalate, etc., we have:

$$E_{EB} = \varepsilon_{0B} - \frac{0.0591}{3}(p_S - \log 2) = \varepsilon_{0B} + 0.006 - \frac{0.0591}{3}p_S.$$

$$E_{EA} = \varepsilon_{0A} + \frac{0.0591}{6}(p_S + 2\log 2) = \varepsilon_{0A} + 0.006 + \frac{0.0591}{6}p_S.$$

If B is univalent and A is quadrivalent, as in case of silver ferrocyanide, we find:

$$E_{EB} = \varepsilon_{0B} - \frac{0.0591}{5}(p_S - \log 4) = \varepsilon_{0B} + 0.007 - \frac{0.0591}{5}p_S.$$

$$E_{EA} = \varepsilon_{0A} + \frac{0.0591}{20}(p_S + 4\log 4) = \varepsilon_{0A} + 0.007 + \frac{0.0591}{20}p_S.$$

**2. Change of the Ion Concentration, or Ion Exponent, and of the Electrode Potential, during a Precipitation Reaction.**—Since we are considering the general course of the titration curve during a precipitation reaction, we assume for the sake of simplicity that the volume of the solution does not change during the titration. This assumption does not introduce any appreciable error at the point where the rapid change in the ion concentration takes place, i.e., at the equivalence-point. We shall start with the simplest case, that of the titration of one univalent ion with another.

For example, let us titrate 0.1 N silver nitrate with chloride in such a way that the volume remains unchanged. Since the silver nitrate is a strong electrolyte, the silver-ion concentration is equal to 0.1 N, or $p_{\text{Ag}} = 1$, at the beginning of the titration. After the precipitation of 90 per cent of the silver as chloride, the silver nitrate concentration is 0.01 N; $[\text{Ag}^+] = 10^{-2}$, or $p_{\text{Ag}} = 2$. By the precipitation of 90 per cent of the silver, $p_{\text{Ag}}$ has only increased by 1, and the potential of the silver electrode has therefore decreased by 59.1 millivolts. After the precipitation of 99 per cent of the silver: $[\text{Ag}^+] = 10^{-3}$, $p_{\text{Ag}} = 3$; for 99.9 per cent of the silver, $[\text{Ag}^+] = 10^{-4}$, $p_{\text{Ag}} = 4$. If we now add the last 0.1 per cent of chloride we have a saturated solution of silver chloride, where $[\text{Ag}^+] = \sqrt{\text{S}}$, or $p_{\text{Ag}} = \frac{1}{2}p_{\text{S}}$.

Since $\text{S}_{\text{AgCl}}$ is about $10^{-10}$, the $[\text{Ag}^+]$ in this saturated solution is $10^{-5}$, and $p_{\text{Ag}} = 5$. It is easy to calculate the change in $[\text{Ag}^+]$, $p_{\text{Ag}}$, and electrode potential, that would be made by successive additions of chloride in excess. The changes of ion concentration, ion exponent, and potential are represented in the following table. The potential values are referred to the original value in 0.1 N solution.

Titration of 0.1 N Silver Nitrate with Chloride. $\text{S}_{\text{AgCl}} = 10^{-10}$

| Per Cent Ag Precipitated | $[\text{Ag}^+]$ | $p_{\text{Ag}}$ | $E_{\text{Ag}}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 0 | $10^{-1}$ | 1 | $a$ | |
| 90 | $10^{-2}$ | 2 | $a-0.059$ | |
| 99 | $10^{-3}$ | 3 | $a-2\times0.059$ | 7 |
| 99.9 | $10^{-4}$ | 4 | $a-3\times0.059$ | 66 |
| 100 | $10^{-5}$ | 5 | $a-4\times0.059$ | 590 |
| Excess of Cl⁻ Per Cent | | | | |
| 0.1 | $10^{-6}$ | 6 | $a-5\times0.059$ | 66 |
| 1 | $10^{-7}$ | 7 | $a-6\times0.059$ | 7 |
| 10 | $10^{-8}$ | 8 | $a-7\times0.059$ | |

In Fig. 5, the change in $p_{Ag}$, or in the potential, is plotted against the percentage of silver precipitated. The left-hand ordinate gives the $p_{Ag}$ values, while the right hand one gives the corresponding change in the potential. For each change of 1 in $p_{Ag}$ there is a change of 59.1 millivolts in the potential. The abscissas give the percentage of the silver precipitated. The point where $p_{Ag} = \frac{1}{2}p_S$ is the equivalence-point; the potential here is $E_{EB}$. As we see from the curve and the table, there is a sudden jump in the potential at the equivalence-point. The greatest change in potential or in ion exponent upon the addition of a little silver nitrate, or chloride, occurs at this point. If we express the change of potential in millivolts as a function of the amount of reagent added, i.e., if we calculate the differ-

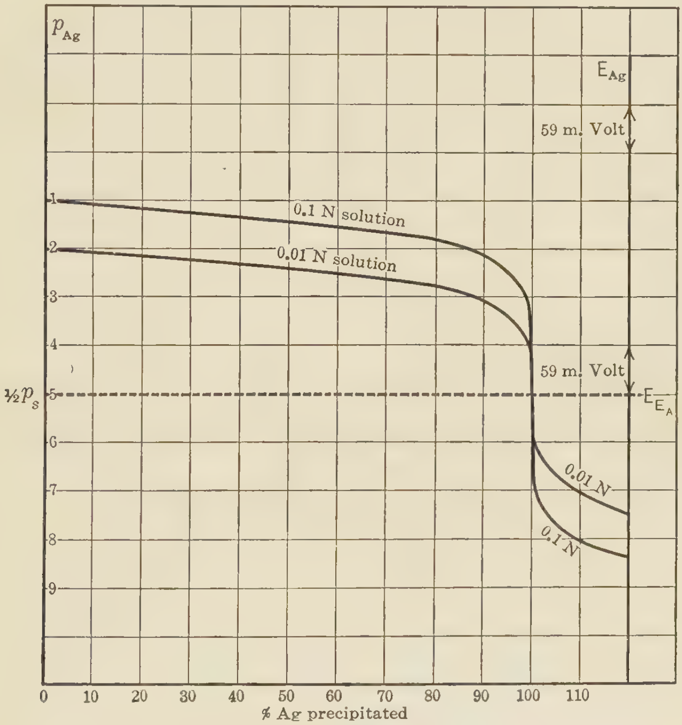

FIG. 5.—Precipitation of silver chloride.

ential quotient $\frac{\Delta E}{\Delta c}$, $c$ being referred to 1 cc. of reagent, *we find a maximum value of* $\frac{\Delta E}{\Delta c}$ *exactly at the equivalence-point.* The "break," or jump[2] in the potential, and also the accuracy of the titration, are dependent upon the magnitude of this quotient. The larger it is, the more accurate the titration.

The magnitude of $\frac{\Delta E}{\Delta c}$ is dependent upon the concentration of the solution to be titrated, and upon the solubility product of the precipitate that is formed. The more concentrated the solution, and the smaller the solubility product, the greater is the jump in the potential, and in the value of $\frac{\Delta E}{\Delta c}$, at the equivalence-point.

In the following table are given the changes during the titration of 0.01 N silver solution with chloride. It is not permissible to neglect the influence of solubility upon the total ion concentration near the equivalence-point. The authors have calculated the correction, $x$, according to equation (12). (See Chapter I, p. 5.)

Titration of 0.01 N Silver Nitrate with Chloride. $S_{AgCl}=10^{-10}$

| Per Cent Ag Precipitated | $[Ag^+]$ | $p_{Ag}$ | $E_{Ag}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 0 | $10^{-2}$ | 2 | $\varepsilon_{0Ag}-1 \times 0.059$ | |
| 90 | $10^{-3}$ | 3 | $\varepsilon_{0Ag}-2 \times 0.059$ | 7 |
| 99 | $10^{-4}$ | 4 | $\varepsilon_{0Ag}-3 \times 0.059$ | 52 |
| 99.9 | $1.6\times10^{-5}$ | 4.80 | $\varepsilon_{0Ag}-3.8\times 0.059$ | 118 |
| 100 | $10^{-5}$ | 5 | $\varepsilon_{0Ag}-4 \times 0.059$ | 118 |
| 100.1 | $6.4\times10^{-6}$ | 5.2 | $\varepsilon_{0Ag}-4.2\times 0.059$ | 52 |
| 101 | $10^{-6}$ | 6 | $\varepsilon_{0Ag}-5 \times 0.059$ | 7 |
| 110 | $10^{-7}$ | 7 | $\varepsilon_{0Ag}-6 \times 0.059$ | |

(*Cf.* the curve in Fig. 5.)

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[2] In most cases, the authors will use the expression "jump" for the sharp rise or fall in the potential in the neighborhood of the equivalence-point. "Break" has been used to describe this phenomenon by Willard and Fenwick, J. Am. Chem. Soc., **44**, 2504 (1922).

In order to demonstrate the influence of solubility product, the authors give, in the following table, the values for the titration of 0.01 N silver nitrate solution with iodide. The solubility product of silver iodide is $10^{-16}$; hence the silver-ion concentration at the equivalence-point is $10^{-8}$, or $p_{\text{Ag}} = 8$.

TITRATION OF 0.01 N SILVER NITRATE WITH IODIDE. $S_{\text{AgI}} = 10^{-16}$

| Per Cent Ag Precipitated | $[\text{Ag}^+]$ | $p_{\text{Ag}}$ | $E_{\text{Ag}}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 0 | $10^{-2}$ | 2 | $\varepsilon_{0\text{Ag}} - 1 \times 0.059$ | |
| 90 | $10^{-3}$ | 3 | $\varepsilon_{0\text{Ag}} - 2 \times 0.059$ | |
| 99 | $10^{-4}$ | 4 | $\varepsilon_{0\text{Ag}} - 3 \times 0.059$ | 7 |
| 99.9 | $10^{-5}$ | 5 | $\varepsilon_{0\text{Ag}} - 4 \times 0.059$ | 66 |
| 100 | $10^{-8}$ | 8 | $\varepsilon_{0\text{Ag}} - 7 \times 0.059$ | 1770 |
| 100.1 | $10^{-11}$ | 11 | $\varepsilon_{0\text{Ag}} - 10 \times 0.059$ | 1770 |
| 101 | $10^{-12}$ | 12 | $\varepsilon_{0\text{Ag}} - 11 \times 0.059$ | 66 |
| 110 | $10^{-13}$ | 13 | $\varepsilon_{0\text{Ag}} - 12 \times 0.059$ | 7 |

In Fig. 6 the values of $\frac{\Delta E}{\Delta c}$ are plotted as ordinates against the excess of silver, or halide in the vicinity of the equivalence-point.

It is evident from this figure that $\frac{\Delta E}{\Delta c}$ is greater the smaller the solubility of the precipitate and the greater the concentration of the solution to be titrated. If the $\frac{\Delta E}{\Delta c} \sim c$ curve is very flat near the equivalence-point the titration can not give accurate results.

In the instance given, where both ions of BA are univalent, the change of $p_{\text{B}}$, or $\frac{\Delta E}{\Delta c}$, is symmetrical on both sides of the equivalence-point. If we had calculated the corresponding values for halogen-ion concentration instead of $[\text{Ag}^+]$ and $p_{\text{Ag}}$, we should have found exactly the same changes in $\frac{\Delta E}{\Delta c}$.

The reader is referred to W. D. Treadwell[3] for the special characteristics of the precipitation curve of BA in the presence of salts.

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[3] W. D. Treadwell, Helv. Chim. Acta, **2**, 672 (1919).

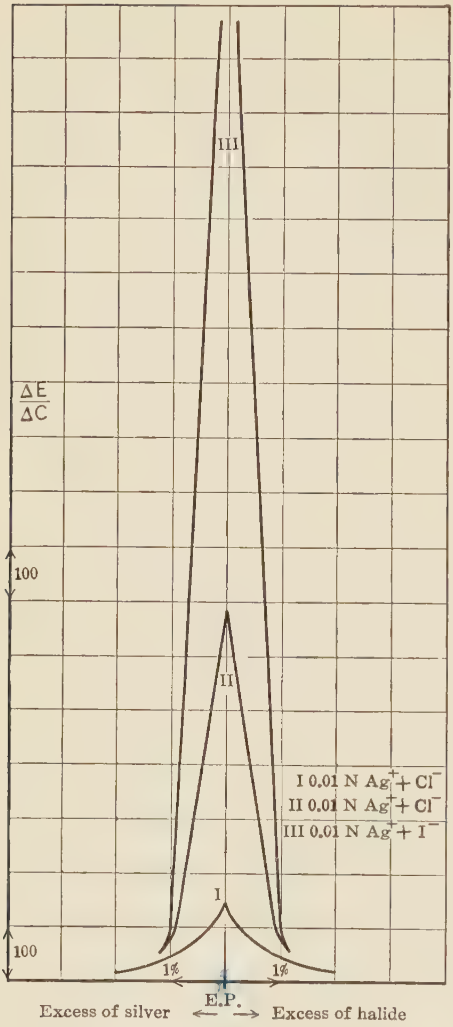

Fig. 6.—Change in $\frac{\Delta E}{\Delta c}$ near the equivalence-point in the precipitation of silver halides.

*The Composition of the Precipitate is* $B_2A$.—If we are titrating a solution of B-ions with a reagent which contains the bivalent ions $A^=$, and if we use the metal B as indicator electrode, the general shape of the precipitation curve will be the same as in the case where BA is formed. In the neighborhood of the equivalence-point, however, there are striking differences, as may be seen from the following table. The variations in the ion exponent and in the electrode potential in the presence of an excess of $B^+$ are quite different from those observed in the presence of an excess of $A^=$; hence the variations in the potential, or better in $\frac{\Delta E}{\Delta c}$, before and after reaching the equivalence-point are not the same.

An illustration will serve to demonstrate this point. Suppose we have a 0.1 N silver solution which we are titrating with an oxalate solution. Assume that the volume remains unchanged during the titration. The solubility product is $10^{-12}$. The reader is referred to Chapter I, p. 5, for the method of calculating the ion concentrations near the equivalence-point.

Titration of 0.1 N Silver Nitrate with Oxalate. $S=10^{-12}$

| Per Cent Ag Precipitated | $[Ag^+]$ | $p_{Ag}$ | $E_{Ag}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 0 | $10^{-1}$ | 1 | $\varepsilon_{0Ag}-1 \times 0.059=\varepsilon_{0Ag}-0.059$ | |
| 90 | $10^{-2}$ | 2 | $\varepsilon_{0Ag}-2 \times 0.059=\varepsilon_{0Ag}-0.118$ | |
| 99 | $10^{-3}$ | 3 | $\varepsilon_{0Ag}-3 \times 0.059=\varepsilon_{0Ag}-0.177$ | |
| 99.7 | $3.2 \times 10^{-4}$ | 3.5 | $\varepsilon_{0Ag}-3.5 \times 0.059=\varepsilon_{0Ag}-0.2065$ | 41 |
| 99.8 | $2.35 \times 10^{-4}$ | 3.63 | $\varepsilon_{0Ag}-3.63 \times 0.059=\varepsilon_{0Ag}-0.2142$ | 77 |
| 99.9 | $1.75 \times 10^{-4}$ | 3.76 | $\varepsilon_{0Ag}-3.76 \times 0.059=\varepsilon_{0Ag}-0.2219$ | 77 |
| 100 | $1.26 \times 10^{-4}$ | 3.90 | $\varepsilon_{0Ag}-3.9 \times 0.059=0\varepsilon_{0Ag}-0.230$ | 81 |
| Excess of | | | | |
| Oxalate | | | | 60 |
| Per Cent | | | | |
| 0.1 | $1 \times 10^{-4}$ | 4 | $\varepsilon_{0Ag}-4 \times 0.059=\varepsilon_{0Ag}-0.236$ | |
| 0.2 | $8.4 \times 10^{-5}$ | 4.08 | $\varepsilon_{0Ag}-4.08 \times 0.059=\varepsilon_{0Ag}-0.241$ | 50 |
| 1 | $3.2 \times 10^{-5}$ | 4.50 | $\varepsilon_{0Ag}-4.5 \times 0.059=\varepsilon_{0Ag}-0.266$ | 31 |

In the following table are represented the corresponding changes of the $A^=$-ion concentration, and of the potential of the A electrode, in the neighborhood of the equivalence-point.

Titration of 0.1 N Silver Nitrate with Oxalate. $S=10^{-12}$

| Per Cent Ag Precipitated | $[A^=]$ | $p_A$ | $E_A$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 99 | $10^{-6}$ | 6 | $\varepsilon_0+3 \times 0.059=\varepsilon_0+0.117$ | |
| 99.7 | $10^{-5}$ | 5 | $\varepsilon_0+2.5 \times 0.059=\varepsilon_0+0.1465$ | 42 |
| 99.8 | $1.75 \times 10^{-5}$ | 4.76 | $\varepsilon_0+2.38 \times 0.059=\varepsilon_0+0.140$ | 65 |
| 99.9 | $3.75 \times 10^{-5}$ | 4.43 | $\varepsilon_0+2.215 \times 0.059=\varepsilon_0+0.131$ | 90 |
| 100 | $6.3 \times 10^{-5}$ | 4.20 | $\varepsilon_0+2.10 \times 0.059=\varepsilon_0+0.124$ | 70 |
| Excess of $A^=$ | | | | 60 |
| Per Cent | | | | |
| 0.1 | $1 \times 10^{-4}$ | 4 | $\varepsilon_0+2 \times 0.059=\varepsilon+0.118$ | |
| 0.2 | $1.42 \times 10^{-4}$ | 3.85 | $\varepsilon_0+1.925 \times 0.059=\varepsilon_0+0.1135$ | 45 |
| 1.0 | $5.2 \times 10^{-4}$ | 3.28 | $\varepsilon_0+1.64 \times 0.059=\varepsilon_0+0.097$ | 20.5 |

Figure 7 represents the changes in $\frac{\Delta E_B}{\Delta c}$ and $\frac{\Delta E_A}{\Delta c}$ near the equivalence-point.

From the table and from Fig. 7, we see that the maximum value of $\frac{\Delta E}{\Delta c}$ *does not appear exactly at the equivalence-point, but appears when there is a small excess of silver ions. If we consider the point where* $\frac{\Delta E}{\Delta c}$ *is a maximum as the end-point, we are introducing an error, which in this instance would be* $=0.2$ *per cent.*

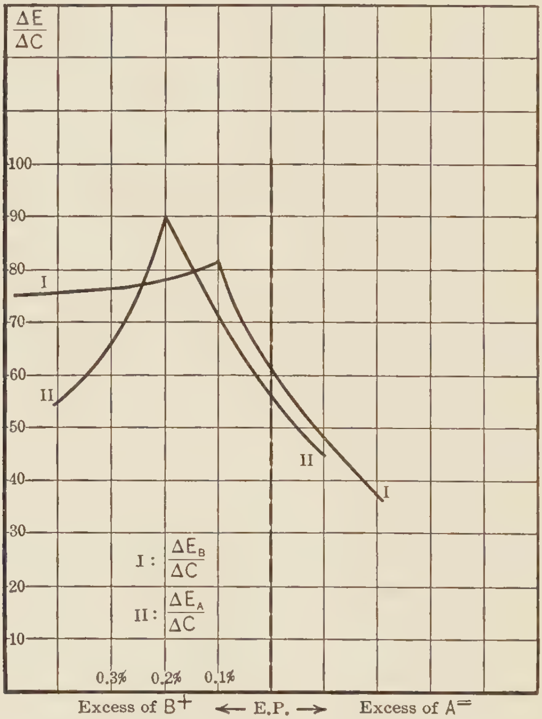

Fig. 7.—$\frac{\Delta E}{\Delta c}$ curves for salts of the type $B_2A$.

The magnitude of this error depends upon the *concentration of the solution to be titrated* and upon the *magnitude of the solubility product.* The error increases with decreasing concentration of the ion to be titrated. If we had used in our example 0.01 N solution instead of 0.1 N, the error would have been about 10 times larger. The error decreases with decreasing value of the solubility product. The smaller the solubility, the sooner it is negligible in comparison with an excess of $B^+$ or of $A^=$. When the solubility is negligible in comparison with the slightest excess of $B^+$ or $A^=$, the maximum value of $\frac{\Delta E}{\Delta c}$ occurs at the equivalence-point.

Theoretically, however, this is never the case. In general, if the slightly soluble substance has the composition $B_xA_y$, the maximum will be found on the $B^+$ side of the equivalence-point when $x$ is greater than $y$, and it will be found on the $A^-$ side when $x$ is less than $y$. In practical cases the error will usually be very small.

The accuracy of the titration is satisfactory only when the solubility is very small in comparison with a small excess of one of the ions. If this is not the case, the changes in the potential, or in $\frac{\Delta E}{\Delta c}$, are very small near the equivalence-point. Therefore, a small error in the determination of the potential may have a great influence upon the determination of the position of the maximum, and the result can not be accurate.

**3. Mathematical Formulation of the Titration Error. Calculation of the Correction for the Titration Error.**[4]—We shall first consider the case in which the precipitate has the composition BA. The ion to be titrated, $B^+$ let us say, has originally the concentration $c$; it will be assumed that the volume remains unchanged during the titration. After the addition of an amount of $A^-$ corresponding to a concentration $y$, there is left in the solution an amount of $B^+$ equal to $(c - y)$. If the solubility of BA is $x$ under these conditions, we have:

$$(c - y + x)x = S. \quad . \quad . \quad . \quad . \quad . \quad (185)$$

S being the solubility product of BA. We also know that the potential of the electrode changes according to the equation:

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[4] The authors wish to thank Dr. A. L. Th. Moesveld, of the van't Hoff Laboratory, Utrecht, for his help in the derivation of the equations in this section.

$$E_B = \varepsilon_{0B} - A \log (c - y + x). \quad . \quad . \quad . \quad (186)$$

A being 0.0591 at 25° C.

Now, we wish to know when the differential quotient $\frac{\Delta E}{\Delta c}$ will reach a maximum. Upon differentiation with respect to $y$ we have:

$$\frac{dE}{dy} = \frac{A}{(c - y + x)}\left(-1 + \frac{x}{c - y + 2x}\right) = -\frac{A}{(c - y + 2x)}.$$

According to equation (185), we have:

$$(c - y + x) = \frac{S}{x};$$

hence:

$$\frac{dE}{dy} = -\frac{A}{\frac{S}{x} + x}. \quad . \quad . \quad . \quad . \quad (187)$$

If we let $\frac{dE}{dy} = V$, we have, upon differentiation with respect to $x$:

$$\frac{dV}{dx} = -\frac{S}{x^2} + 1.$$

This term is a maximum when: $-\frac{S}{x^2} + 1 = 0$, or when

$$x = \sqrt{S}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (188)$$

Hence, in case the precipitate has the composition BA, the maximum value of $\frac{dE}{dc}$ will be found exactly at the equivalence-point.

We shall now consider the case in which the composition of the precipitate is $B_2A$.

$B^+$ originally has the concentration $c$; after the addition of an amount of $A^=$ equivalent to a normality of $y$, there is left in solution an amount of B corresponding to a concentration of

$(c - y)$. If the solubility of $B_2A$ under these conditions is equal to $\frac{1}{2}x$, we have $[B^+] = (c - y + x)$, and $[A^-] = \frac{1}{2}x$, and

$$(c - y + x)^2 \tfrac{1}{2}x = S. \quad \text{. . . . . . . . . .} \quad (189)$$

S being the solubility product of $B_2A$.

Moreover, we have again:

$$E_B = \varepsilon_{0B} - A \log (c - y + x). \quad . \quad (186)$$

Differentiation with respect to $y$ yields:

$$\frac{dE}{dy} = \frac{A}{(c - y + x)}\left(-1 + \frac{2x}{2x + (c - y + x)}\right)$$

$$= -\frac{A}{2x + (c - y + x)}.$$

According to (189):

$$(c - y + x) = \sqrt{\frac{2S}{x}},$$

and

$$V = \frac{dE}{dy} = -\frac{A}{2x + \sqrt{\frac{2S}{x}}}.$$

Differentation with respect to $x$ gives:

$$\frac{dV}{dx} = 2x + \sqrt{\frac{2S}{x}}.$$

$dV$ will reach its maximum when $\frac{d}{dx}\left(\sqrt{\frac{2S}{x}} + 2x\right) = 0.$

$$4\sqrt{x} - \frac{\sqrt{2S}}{x} = 0, \quad \text{. . . . . . . .} \quad (190)$$

or when:

$$x = \tfrac{1}{2}\sqrt[3]{S}. \quad \text{. . . . . . . .} \quad (191)$$

At the equivalence-point we have:

$$\tfrac{1}{2}x^3 = S,$$

or

$$x = \sqrt[3]{2} \cdot \sqrt[3]{S} = 1.26\sqrt[3]{S}. \quad . \quad (192)$$

From (191) and (192) we see that the maximum value of $\frac{dE}{dy}$

is not reached at the equivalence-point, where $x = 1.26\sqrt[3]{S}$, but at the point where the *solubility is decreased 2.5 times by the excess of B.* It is now very easy to calculate the titration error, i.e., the error which we make by assuming that the maximum value of $\frac{dE}{dc}$ coincides with the position of the equivalence-point. From equation (191) we see that the maximum appears when:

$$x = \tfrac{1}{2}\sqrt[3]{S}.$$

Then $[A^=] = \frac{1}{4}\sqrt[3]{S}$, and we can calculate $[B^+]$ from the equation:

$$[B^+]^2 \cdot \tfrac{1}{4}\sqrt[3]{S} = S,$$

and

$$[B^+] = 2\sqrt[3]{S}.$$

Hence, at the point where the maximum appears, $[B^+]$ is equal to $2\sqrt[3]{S}$, and the excess $b$ of $[B^+]$ is equal to:

$$b = [B^+] - x = 2\sqrt[3]{S} - \tfrac{1}{2}\sqrt[3]{S} = 1\tfrac{1}{2}\sqrt[3]{S}. \quad . \quad . \quad (193)$$

If the volume at the equivalence-point is $v$, we have an excess $b$ of $B^+$, which is:

$$b = \frac{v}{1000} \text{ equivalent.}$$

If the original concentration of $B^+$ is equal to B equivalents, the titration error is:

$$\text{Titration Error} = \frac{b}{B} \cdot \frac{v}{1000} \cdot 100 \text{ per cent}$$

$$= \frac{1.5\sqrt[3]{S}}{B} \cdot \frac{v}{1000} \cdot 100 \text{ per cent}, \quad . \quad (194)$$

and we have to take into consideration the fact that the maximum occurs on the $B^+$-side of the equivalence-point.

*Example.*—Let us consider a simple illustration in which $S = 10^{-12}$. Let the final volume, at the equivalence-point be 100; and $[B^+] = 10^{-2}$. This case occurs when we titrate 0.2 N silver nitrate with 0.1 molar oxalate.

Then we have:

$$b = 1.5\sqrt[3]{S} = 1.5 \times 10^{-4},$$

and

$$\text{Titration Error} = \frac{b}{B} \cdot \frac{v}{1000} \cdot 100 \text{ per cent} = 0.15 \text{ per cent.}$$

From the more or less rough calculation on p. 78 we found that the titration error under the conditions mentioned was about 0.2 per cent.

We learn from equation (194) that the titration error decreases as the value of S decreases, or as the equivalence-point volume decreases, or as the concentration of the ion to be titrated increases.

We shall now consider the general case in which the precipitate has the composition $B_nA_m$.

$$B_nA_m \rightleftarrows nB^+ + mA^-.$$

At the equivalence-point:

$$[B^+] = \frac{n}{m}[A^-],$$

and

$$[B^+]^n[A^-]^m = S_{B_nA_m}.$$

$B^+$ originally has the concentration $c$; after an amount of $A^-$ corresponding to a normality $y$ has been added, there is left in the solution an amount of B corresponding to a normality $(c - y)$. If the solubility of $B_nA_m$ corresponds to a concentration of B-ions equal to $x$, then we have:

$$[B^+] = \frac{1}{m}(c - y) + x,$$

and

$$[A^-] = \frac{m}{n}x,$$

and

$$\left\{\frac{1}{m}(c - y) + x\right\}^n \left(\frac{m}{n}x\right)^m = S_{B_nA_m}.$$

The potential of the electrode changes according to the equation:

$$E_B = \varepsilon_0 - A \log\left\{\frac{1}{m}(c - y) + x\right\}.$$

Then we have:

$$\frac{dy}{dn} = \frac{x}{\frac{m^2}{n}\left\{\frac{1}{m}(c-y)+x\right\}+mx},$$

$$\frac{dE}{dy} = -\frac{A}{m\left\{\frac{1}{m}(c-y)+x\right\}+nx} = -\frac{A}{m\sqrt[n]{\frac{S}{\left(\frac{m}{n}x\right)^m}}}.$$

The position of the maximum is determined by:

$$\frac{d}{dy}\left\{m\sqrt[n]{\frac{S}{\left(\frac{m}{n}x\right)^m}}+nx\right\}$$

or

$$\frac{d}{dx}\left\{m\sqrt[n]{\frac{S}{\left(\frac{m}{n}x\right)^m}}+nx\right\} = 0.$$

From this we have:

$$nx^{\frac{m}{n}+1} = m\frac{m}{n}\left(\frac{m}{n}\right)^{-\frac{m}{n}}S^{\frac{1}{n}},$$

$$x = \frac{n}{m}\sqrt[\frac{m+n}{n}]{\frac{m^3}{n^3}S^{\frac{1}{n}}}.$$

This last equation gives us an expression for the magnitude of the solubility at the point where $\frac{\Delta E}{\Delta c}$ has a maximum value.

By applying this equation, we have for the case $n = 2$, $m = 1$, (salt $B_2A$):

$$x = \tfrac{1}{2}\sqrt[3]{S}.$$

**4. Titration of One Ion in the Presence of Another, When Both Ions May Form Insoluble Compounds with the Reagent.**—If we have in a solution two anions, $A^-$ and $A_1{}^-$, both of which may form sparingly soluble salts, BA and $BA_1$, respectively, then the salt $BA_1$ will be first precipitated upon the addition of $B^+$, if it is the less soluble of the two salts. (*Cf.* p. 13*ff*, Chapter I.)

As we have seen (p. 13), only the salt $BA_1$ will be precipitated as long as:

$$\frac{[A_1^-]}{[A^-]} > \frac{S_{BA_1}}{S_{BA}}. \quad \ldots\ldots \quad (31)$$

When the ratio between the concentrations of the two ions is equal to the ratio of their solubility products, the second salt, BA, will begin to be precipitated, and the ratio between the concentrations of the two anions thereafter will remain constant.

The precipitation and potential curves for the titration of $A_1^-$ in the presence of $A^-$ will have the same shape as if the former alone were present in the solution, except in the immediate neighborhood of the equivalence-point. In the absence of $A^-$-ion, the $A_1^-$-ion concentration is equal to $\sqrt{S_{BA_1}}$ at the equivalence-point; it then diminishes rapidly with a slight excess of $B^+$-ion. In the presence of $A^-$-ion, the $A_1^-$-ion concentration decreases just before the equivalence-point to:

$$[A_1^-] = [A^-]\frac{S_{BA_1}}{S_{BA}}.$$

When this concentration of $A_1^-$ is reached, a further addition of $B^+$-ions changes the $A_1^-$- and $A^-$-ion concentration very slightly. The jump in the potential and the maximum value of $\frac{\Delta E}{\Delta c}$ occur too early; there is always a trace of $A_1^-$ left in the solution when BA begins to be precipitated.

The titration error is equal to:

$$\text{Titration Error} = [A^-]\frac{S_{BA_1}}{S_{BA}} \cdot \frac{v}{1000} \cdot \frac{1}{A} \cdot 100 \text{ per cent.} \quad (195)$$

$v$ is the volume at the first equivalence-point; A is the number of equivalents of $A^-$ that were originally present in the solution. As in all other cases, the titration error increases with increasing values of $v$ and with decreasing values of A. We see also that the titration error increases with increasing values of $[A^-]$, and with increasing values of the ratio between the solubility products of $BA_1$ and BA. Hence, the greater the concentration of the ion that forms the more soluble compound, and the smaller the difference between the solubility products of the two substances, the less accurate is the titration.

*Examples.*—We have 50 cc. of a mixture of 0.1 N $I^-$ and 0.1 N $Cl^-$, which we are titrating with 0.1 N silver nitrate. At the first equivalence-point, where silver chloride begins to be precipitated, $v$ is equal to 100. Furthermore, we have

$$A = \frac{0.01}{2}. \quad S_{AgI} = 10^{-16}. \quad S_{AgCl} = 10^{-12}.$$

$$\text{Titration Error} = 10^{-1}\cdot\frac{10^{-16}}{10^{-12}}\cdot\frac{1}{10}\cdot\frac{200}{1}\cdot 100 \text{ per cent}$$

$$= 2 \times 10^{-4} \text{ per cent.}$$

If the iodide concentration had been 0.01 N, and that of the chloride 1 N, then

$$\text{Titration Error} = 2 \times 10^{-3} \text{ per cent.}$$

If we have a mixture of 0.1 N $I^-$ and 0.1 N $Br^-$, we use the solubility products of silver iodide and silver bromide in the calculation.

$$S_{AgI} = 10^{-16}. \qquad S_{AgBr} = 5 \times 10^{-13}.$$

$$\text{Titration Error} = 10^{-1}\cdot\frac{10^{-16}}{5 \times 10^{-13}}\cdot\frac{1}{10}\cdot\frac{200}{1}\cdot 100 \text{ per cent}$$

$$= 0.04 \text{ per cent.}$$

The precipitation of the silver bromide begins when the iodide concentration has become $2 \times 10^{-5}$.

If we had taken a mixture of 0.01 N iodide and 1 N bromide, then:

$$\text{Titration Error} = 1\cdot\frac{10^{-16}}{5 \times 10^{-13}}\cdot\frac{1}{10}\cdot 2000\cdot 100 \text{ per cent}$$

$$= 4 \text{ per cent.}$$

In the following table is given the change in the silver-ion concentration, in the $p_{Ag}$, in the potential of the silver electrode, and in $\frac{\Delta E}{\Delta c}$ for a mixture of 0.01 N iodide and 0.01 N bromide. For the sake of simplicity it is again assumed that the volume remains unchanged.

TITRATION OF A MIXTURE 0.01 N WITH RESPECT TO $I^-$ AND TO $Br^-$ WITH $Ag^+$

Total Volume, 100 cc. $S_{AgI}=10^{-16}$. $S_{AgBr}=5\times10^{-13}$

| Per Cent $I^-$ Precipitated | $[Ag^+]$ | $p_{Ag}$ | $E_{Ag}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 90 | $10^{-13}$ | 13 | $\varepsilon_0-13\times0.059=\varepsilon_0-0.767$ | |
| 99 | $10^{-12}$ | 12 | $\varepsilon_0-12\times0.059=\varepsilon_0-0.708$ | 56 |
| 99.8 | $5\times10^{-12}$ | 11.3 | $\varepsilon_0-11.3\times0.059=\varepsilon_0-0.667$ | 180 |
| 99.9 | $10^{-11}$ | 11 | $\varepsilon_0-11\times0.059=\varepsilon_0-0.649$ | 410 |
| Per Cent $Br^-$ Precipitated | | | | |
| 0.01 | $5\times10^{-11}$ | 10.3 | $\varepsilon_0-10.3\times0.059=\varepsilon_0-0.608$ | 0 |
| 0.1 | $5\times10^{-11}$ | 10.3 | $\varepsilon_0-10.3\times0.059=\varepsilon_0-0.608$ | |
| 90 | $5\times10^{-10}$ | 9.3 | $\varepsilon_0-9.3\times0.059=\varepsilon_0-0.549$ | |
| 99 | $5\times10^{-9}$ | 8.3 | $\varepsilon_0-8.3\times0.059=\varepsilon_0-0.490$ | 52 |
| 99.8 | $2.5\times10^{-8}$ | 7.6 | $\varepsilon_0-7.6\times0.059=\varepsilon_0-0.448$ | 170 |
| 99.9 | $5\times10^{-8}$ | 7.3 | $\varepsilon_0-7.3\times0.059=\varepsilon_0-0.431$ | 680 |
| 100 | $7\times10^{-7}$ | 6.16 | $\varepsilon_0-6.16\times0.059=\varepsilon_0-0.363$ | 680 |
| Excess of Silver Per Cent | | | | |
| 0.1 | $10^{-5}$ | 5 | $\varepsilon_0-5\times0.059=\varepsilon_0-0.295$ | 170 |
| 0.2 | $2\times10^{-5}$ | 4.7 | $\varepsilon_0-4.7\times0.059=\varepsilon_0-0.277$ | 52 |
| 1.0 | $10^{-4}$ | 4 | $\varepsilon_0-4\times0.059=\varepsilon_0-0.236$ | |

Figure 8 represents the precipitation curve. The first inflection corresponds to the point where practically all of the iodide has been precipitated; the second jump in the potential corresponds to the point where all of the bromide is precipitated. The dotted line represents the course of the curve when 0.01 N $I^-$ is titrated in the absence of bromide. As may be seen from the graph, the first jump in potential is decreased to a marked degree in the presence of bromide. The second jump, where the precipitation of the bromide is complete, is exactly the same as in the absence of iodide.

If one of the ions is univalent and the other bivalent, giving the insoluble compounds $BA_1$ and $B_2A$, $BA_1$ being the less soluble compound, the precipitation of the second salt begins when:

$$[A_1^-] = \frac{S_{BA_1}}{\sqrt{S_{B_2A}}}[A^=].$$

We may readily calculate the electrode potential at the first equivalence-point from this equation.

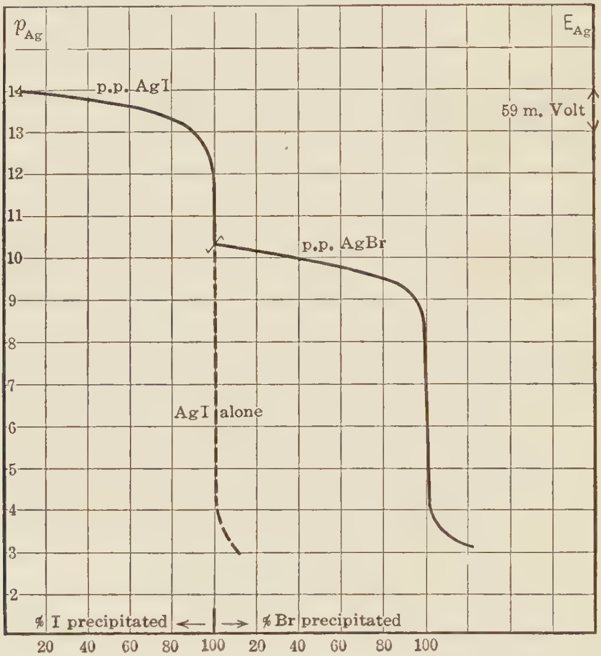

FIG. 8.—100 cc. of a mixture 0.01 N in both $I^-$ and $Br^-$ titrated with 0.01 $NAg^+$.

**5. Neutralizations.**—When we titrate a strong acid with a strong base we are dealing with strong electrolytes. The neutralization curve may then be compared with the precipitation curve in the case where the slightly soluble simple compound BA is formed. Instead of the solubility product we deal with the ion product of water in neutralizations.

$$[H^+][OH^-] = K_w. \quad (\textit{Cf.}\ \text{p. 19, equation (41).})$$

At the equivalence-point $p_{\text{H}} = \frac{1}{2}p_{\text{H}_2\text{O}}$; at room temperature $\frac{1}{2}p_{\text{H}_2\text{O}} = 7$.

The theoretical value of the potential of the hydrogen electrode at the equivalence-point in the titration of a strong acid with a strong base is:

$$E_{\text{H}} = \varepsilon_{0\text{H}} - 7 \times 0.059.$$

Practically, we find that the maximum is usually at a smaller value of $p_{\text{H}}$ rather than at $p_{\text{H}} = 7$, owing to impurities, especially carbonic acid, which are present in the solutions. When the carbonic acid content is rather large, we find two jumps in the potential, one at $p_{\text{H}} = 4 - 5$, and the other at about $p_{\text{H}} = 8$.

The theoretical shape of the neutralization curve may be pictured from the data in the following table. As usual, it is assumed that the volume is constant at 100 cc.

Titration of 100 cc. of 0.01 N Hydrochloric Acid with Sodium Hydroxide $Kw = 10^{-7}$

| Per Cent Neutralized | $[\text{H}^+]$ | $p_{\text{H}}$ | $E_{\text{H}_2}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 0 | $10^{-2}$ | 2 | $\varepsilon_0 - 2 \times 0.059$ | |
| 90 | $10^{-3}$ | 3 | $\varepsilon_0 - 3 \times 0.059$ | |
| 99 | $10^{-4}$ | 4 | $\varepsilon_0 - 4 \times 0.059$ | |
| 99.9 | $10^{-5}$ | 5 | $\varepsilon_0 - 5 \times 0.059$ | 65 |
| 100 | $10^{-7}$ | 7 | $\varepsilon_0 - 7 \times 0.059$ | |
| Excess of NaOH | | | | 1180 |
| Per Cent | | | | 1180 |
| 0.1 | $10^{-9}$ | 9 | $\varepsilon_0 - 9 \times 0.059$ | |
| 1 | $10^{-10}$ | 10 | $\varepsilon_0 - 10 \times 0.059$ | 65 |
| 10 | $10^{-11}$ | 11 | $\varepsilon_0 - 11 \times 0.059$ | |

The neutralization curve of 0.01 N hydrochloric acid is shown in Fig. 9.

The change in the neutralization curve and also in $\frac{\Delta E}{\Delta c}$ is exactly the same just before and just after the equivalence-point, which occurs exactly at $p_{\text{H}} = 7$. This is no longer the case when we titrate a weak acid with a strong base, or a weak base with a strong acid. In the former case the equivalence-point is found in alkaline solution, in the latter case in acid solution, because of hydrolysis.

From the considerations given in Chapter I, § 5-§ 9, it is easy to construct the neutralization curve. From equation (64) we know that in the titration of a weak acid with a strong base the equivalence-point will be found at:

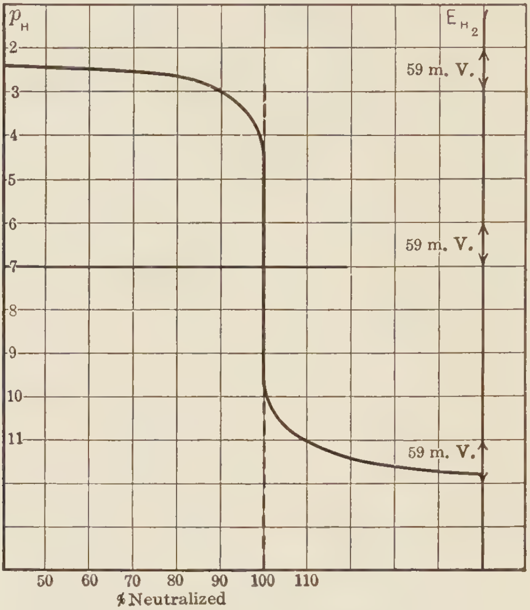

FIG. 9.—Neutralization curve, 0.01 N HCl with NaOH.

$$p_H = 7 + \tfrac{1}{2}p_a + \tfrac{1}{2}\log c. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (64)$$

The potential of the hydrogen electrode will then be:

$$E_{H_2} = \varepsilon_0 - 0.059(7 + \tfrac{1}{2}p_a + \tfrac{1}{2}\log c).$$

In the titration of a weak base with a strong acid, the $p_H$ at the equivalence-point is:

$$p_H = 7 - \tfrac{1}{2}p_b - \tfrac{1}{2}\log c. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (62)$$

and the electrode potential is:

$$E_{H_2} = \varepsilon_{0H_2} - 0.059(7 - \tfrac{1}{2}p_b - \tfrac{1}{2}\log c).$$

In the following table are given the data for the titration of 0.1 N acetic acid. It is again assumed that the volume of the solution remains constant during the titration.

TITRATION OF 0.1 N ACETIC ACID WITH SODIUM HYDROXIDE
$K_a = 1.8 \times 10^{-5}$. $K_w = 10^{-14}$

| Per Cent Neutralized | $[H^+]$ | $p_H$ | $E_{H_2}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 0 | $1.35 \times 10^{-3}$ | 2.87 | $\varepsilon_0 - 2.87 \times 0.059 = \varepsilon_0 - 0.170$ | |
| 10 | $1.6 \times 10^{-4}$ | 3.80 | $\varepsilon_0 - 3.80 \times 0.059 = \varepsilon_0 - 0.224$ | |
| 50 | $1.8 \times 10^{-5}$ | 4.75 | $\varepsilon_0 - 4.75 \times 0.059 = \varepsilon_0 - 0.280$ | |
| 90 | $2.0 \times 10^{-6}$ | 5.70 | $\varepsilon_0 - 5.70 \times 0.059 = \varepsilon_0 - 0.336$ | |
| 99 | $1.8 \times 10^{-7}$ | 6.75 | $\varepsilon_0 - 6.75 \times 0.059 = \varepsilon_0 - 0.398$ | |
| 99.8 | $3.6 \times 10^{-8}$ | 7.45 | $\varepsilon_0 - 7.45 \times 0.059 = \varepsilon_0 - 0.440$ | 52 |
| 99.9 | $1.8 \times 10^{-8}$ | 7.75 | $\varepsilon_0 - 7.75 \times 0.059 = \varepsilon_0 - 0.457$ | 170 |
| 100 | $1.35 \times 10^{-9}$ | 8.87 | $\varepsilon_0 - 8.87 \times 0.059 = \varepsilon_0 - 0.523$ | 660 |
| Excess of NaOH Per Cent | | | | 670 |
| 0.1 | $10^{-10}$ | 10 | $\varepsilon_0 - 10 \times 0.059 = \varepsilon_0 - 0.590$ | |
| 0.2 | $5 \times 10^{-11}$ | 10.3 | $\varepsilon_0 - 10.3 \times 0.059 = \varepsilon_0 - 0.610$ | 200 |
| 1 | $10^{-11}$ | 11 | $\varepsilon_0 - 11 \times 0.059 = \varepsilon_0 - 0.649$ | 49 |

When the degree of hydrolysis is not negligible near the equivalence-point, we must use equations (65) and (66) for the exact calculation of $p_H$. This has been done in the two following examples. We assume that the volume remains constant: Solution 0.1 N; $K_a = 10^{-7}$, or $10^{-9}$, respectively.

The maximum is found practically at the equivalence-point. There are indeed two maxima, one at either side of the equivalence-point and very close to it. We observe only one maximum at the equivalence-point in those cases which give satisfactory practical results. As may be seen from the data and the curves, the magnitude of $\frac{\Delta E}{\Delta c}$ decreases with decreasing dissocia-

Titration of 0.1 N Acid with Sodium Hydroxide. $K_a=10^{-7}$. $K_w=10^{-14}$

| Per Cent Neutralized | H | $p_H$ | $E_{H_2}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 0 | $10^{-4}$ | 4 | $\varepsilon_0 - 4 \times 0.059 = \varepsilon_0 - 0.236$ | |
| 9 | $10^{-6}$ | 6 | $\varepsilon_0 - 6 \times 0.059 = \varepsilon_0 - 0.354$ | |
| 50 | $10^{-7}$ | 7 | $\varepsilon_0 - 7 \times 0.059 = \varepsilon_0 - 0.413$ | |
| 91 | $10^{-8}$ | 8 | $\varepsilon_0 - 8 \times 0.059 = \varepsilon_0 - 0.472$ | |
| 99 | $10^{-9}$ | 9 | $\varepsilon_0 - 9 \times 0.059 = \varepsilon_0 - 0.531$ | |
| 99.8 | $2.4 \times 10^{-10}$ | 9.62 | $\varepsilon_0 - 9.62 \times 0.059 = \varepsilon_0 - 0.568$ | 46 |
| 99.9 | $1.64 \times 10^{-10}$ | 9.785 | $\varepsilon_0 - 9.785 \times 0.059 = \varepsilon_0 - 0.577$ | 90 |
| 100 | $10^{-10}$ | 10 | $\varepsilon_0 - 10 \times 0.059 = \varepsilon_0 - 0.590$ | 130 |
| Excess of NaOH, Per Cent | | | | 130 |
| 0.1 | $6.2 \times 10^{-11}$ | 10.215 | $\varepsilon_0 - 10.215 \times 0.059 = \varepsilon_0 - 0.603$ | |
| 0.2 | $4.2 \times 10^{-11}$ | 10.38 | $\varepsilon_0 - 10.38 \times 0.059 = \varepsilon_0 - 0.612$ | 90 |
| 1.0 | $10^{-11}$ | 11 | $\varepsilon_0 - 11 \times 0.059 = \varepsilon_0 - 0.649$ | 46 |

Titration of 0.1 N Acid with Sodium Hydroxide. $K_a=10^{-9}$. $K_w=10^{-14}$

| Per Cent Neutralized | $[H^+]$ | $p_H$ | $E_{H_2}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 0 | $10^{-5}$ | 5 | $\varepsilon_0 - 5 \times 0.059 = \varepsilon_0 - 0.295$ | |
| 9 | $10^{-8}$ | 8 | $\varepsilon_0 - 8 \times 0.059 = \varepsilon_0 - 0.472$ | |
| 50 | $10^{-9}$ | 9 | $\varepsilon_0 - 9 \times 0.059 = \varepsilon_0 - 0.531$ | |
| 91 | $10^{-10}$ | 10 | $\varepsilon_0 - 10 \times 0.059 = \varepsilon_0 - 0.590$ | |
| 99 | $1.62 \times 10^{-11}$ | 10.79 | $\varepsilon_0 - 10.79 \times 0.059 = \varepsilon_0 - 0.6365$ | |
| 99.7 | $1.16 \times 10^{-11}$ | 10.934 | $\varepsilon_0 - 10.934 \times 0.059 = \varepsilon_0 - 0.6450$ | 12 |
| 99.8 | $1.10 \times 10^{-11}$ | 10.954 | $\varepsilon_0 - 10.954 \times 0.059 = \varepsilon_0 - 0.6463$ | 13 |
| 99.9 | $1.05 \times 10^{-11}$ | 10.978 | $\varepsilon_0 - 10.978 \times 0.059 = \varepsilon_0 - 0.6477$ | 14 |
| 100 | $10^{-11}$ | 11 | $\varepsilon_0 - 11 \times 0.059 = \varepsilon_0 - 0.649$ | 13 |
| Excess of NaOH Per Cent | | | | 12 |
| 0.1 | $9.5 \times 10^{-12}$ | 11.021 | $\varepsilon_0 - 11.021 \times 0.059 = \varepsilon_0 - 0.6502$ | |
| 0.2 | $9 \times 10^{-12}$ | 11.041 | $\varepsilon_0 - 11.041 \times 0.059 = \varepsilon_0 - 0.6514$ | 12 |
| 1 | $6.1 \times 10^{-12}$ | 11.21 | $\varepsilon_0 - 11.21 \times 0.059 = \varepsilon_0 - 0.662$ | 12.5 |

tion constant of the acid. A simple calculation shows us also that the magnitude decreases with decrease in the concentration of the acid that is to be titrated.

In the titration of the acid of dissociation constant $10^{-9}$ at a concentration of 0.1 N, there is no sharp end-point. (*Cf.* table opp.) The inflection is very small. An error of 1 millivolt in the determination of the electrode potential would have a great influence on the position of the maximum. Such a titration can not give accurate results. The practical limit is reached, when $K_a$ equals $10^{-8}$, at a concentration of 0.1 N. Acids with smaller dissociation constants can not be titrated accurately at concentrations smaller than 0.1 N.

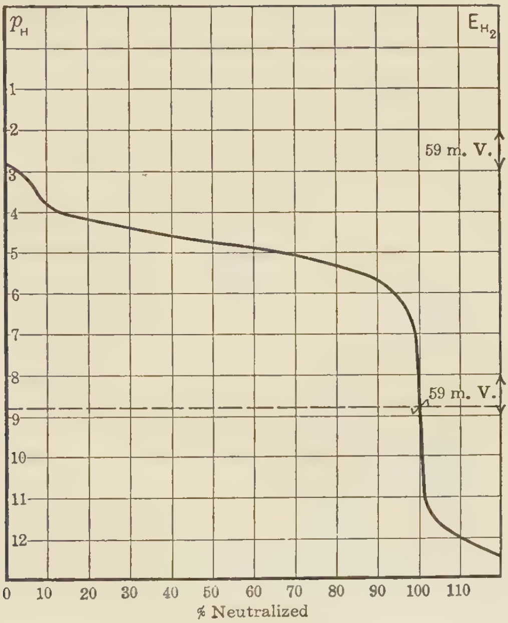

FIG. 10.—Neutralization curve, 0.1 N acetic acid with sodium hydroxide.

When the dissociation constant of the acid is very small, there is no inflection-point at all. In a recent paper E. D. Eastman[5] has calculated that at 1 N concentration an inflection-point occurs if $K_a$ is greater than $10^{-11}$; not if $K_a$ is equal to $10^{-12}$. At a concentration of $10^{-3}$ the above limit is shifted $10^3$ times, and an inflection-point is found if $K_a$ is greater than $10^{-8}$. Eastman remarks: "The failure of the inflection to appear seems more remarkable when it is considered that, in the case where $c$ equals 1 N and $K_a$ equals $10^{-12}$, only about 10 per cent of the acid would remain undissociated (that is, only 10 per cent of the salt would be hydrolyzed at the end-point)." According to Eastman, the inflection-point and the end-point are at different positions with acids of strength but little more than sufficient to produce an inflection. The error may be 0.3 per cent; the discrepancies decrease rapidly as the strength of the acid is increased. Therefore, in all practical cases, we may consider the inflection-point and the end-point as identical.

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[5] E. D. Eastman, J. Am. Chem. Soc., **47**, 333 (1925).

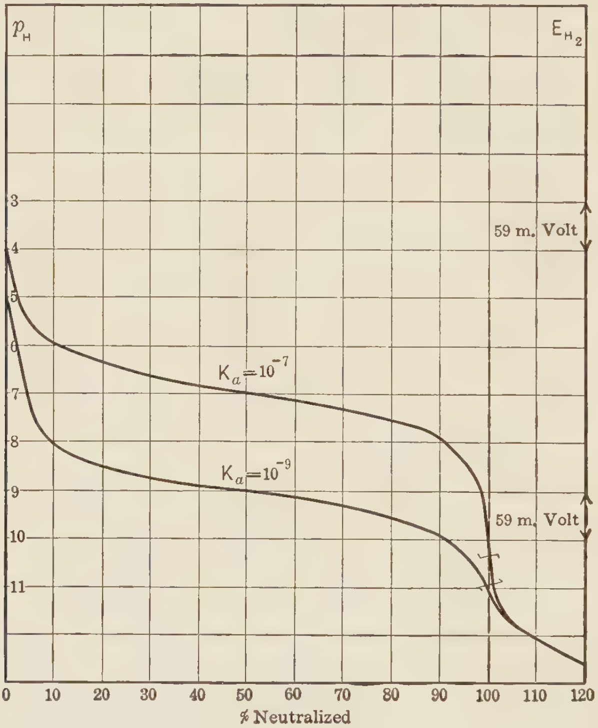

FIG. 11.—Neutralization curves of 0.1N acids of $K_a = 10^{-7}$ and $K_a = 10^{-9}$.

The neutralization curve of a weak acid with a weak base will be the combination of two neutralization curves, namely that of a weak acid and a strong base with that of a weak base and a strong acid. Differences appear at the equivalence-point, which in all practical cases lies at a $p_H$ near 7. Owing to hydrolysis at both sides of this point (*cf.* Chapter I, p. 26) the jump in potential at the equivalence-point will never be very large. At a distance of about 5 per cent from the equivalence-point the neutralization curve coincides with that of a weak acid and a strong base, or with that of a weak base and a strong acid, respectively, since the salts of weak acids and weak bases are strong electrolytes.

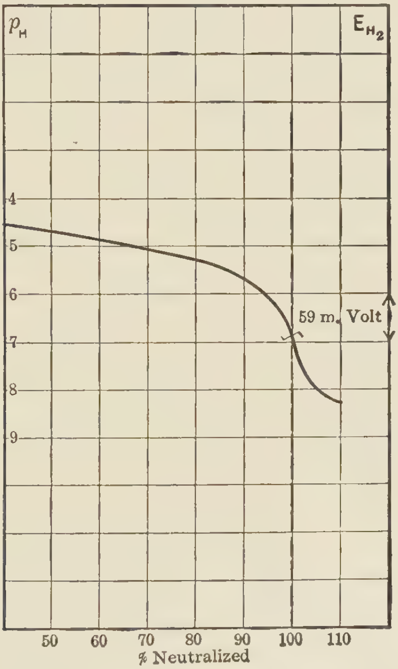

FIG. 12.—Neutralization curve, 0.1 N acetic acid with ammonia.

In the following table are given the values of $p_H$, etc., that are obtained in the neutralization of 0.1 N acetic acid with ammonia. It is assumed that the volume is constant during the titration. Equations (72) and (73) (p. 27) have been used for the calculation of $[H^+]$ in the neighborhood of the equivalence-point.

Titration of 0.1 N Acetic Acid with Ammonia. $K_a=K_b=10^{-4.75}$
$K_w=10^{-14}$

| Per Cent Neutralized | $[H^+]$ | $p_H$ | $E_{H_2}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 50 | $1.8\times10^{-5}$ | 4.75 | $\varepsilon_0-4.75\times0.059=\varepsilon_0-0.280$ | |
| 90 | $2.0\times10^{-6}$ | 5.70 | $\varepsilon_0-5.70\times0.059=\varepsilon_0-0.336$ | |
| 98 | $3.7\times10^{-7}$ | 6.43 | $\varepsilon_0-6.43\times0.059=\varepsilon_0-0.379$ | |
| 99 | $2.2\times10^{-7}$ | 6.65 | $\varepsilon_0-6.65\times0.059=\varepsilon_0-0.392$ | 13 |
| 99.6 | $1.42\times10^{-7}$ | 6.85 | $\varepsilon_0-6.85\times0.059=\varepsilon_0-0.4040$ | 20 |
| 99.8 | $1.20\times10^{-7}$ | 6.923 | $\varepsilon_0-6.923\times0.059=\varepsilon_0-0.4084$ | 22 |
| 99.9 | $1.12\times10^{-7}$ | 6.961 | $\varepsilon_0-6.961\times0.059=\varepsilon_0-0.4106$ | 22 |
| 100 | $1\times10^{-7}$ | 7 | $\varepsilon_0-7\times0.059=\varepsilon_0-0.4130$ | 24 |
| Excess of Ammonia Per Cent | | | | 24 |
| 0.1 | $9.14\times10^{-8}$ | 7.039 | $\varepsilon_0-7.039\times0.059=\varepsilon_0-0.4154$ | |
| 0.2 | $8.38\times10^{-8}$ | 7.077 | $\varepsilon_0-7.077\times0.059=\varepsilon_0-0.4176$ | 22 |
| 0.4 | $7.08\times10^{-8}$ | 7.15 | $\varepsilon_0-7.15\times0.059=\varepsilon_0-0.422$ | 22 |
| 1 | $4.5\times10^{-8}$ | 7.35 | $\varepsilon_0-7.35\times0.059=\varepsilon_0-0.434$ | 20 |
| 2 | $2.7\times10^{-8}$ | 7.57 | $\varepsilon_0-7.57\times0.059=\varepsilon_0-0.447$ | 13 |

As may be seen from the table, we do not find a sharply defined maximum at the equivalence-point. The stronger the acid and the base, the sharper is the maximum. If the acid and base have different strengths, the maximum is not situated exactly at the equivalence-point. It is of no practical significance, however, to calculate the error, since it is negligible in all instances where a pronounced inflection occurs. When the jump in potential is very small the titration can not be very accurate, because an error of 1 millivolt in the determination of the electrode potential will change the position of the maximum appreciably. The titration of 0.1 N acetic acid with ammonia can not be carried out with an accuracy greater than 0.2 per cent.

If the dissociation constant of the acid and base are very small there is no inflection at all at the equivalence-point. The limits are given in the following table:

CONCENTRATION

| | 1N | $10^{-1}$N | $10^{-2}$N | $10^{-3}$N |
|---|---|---|---|---|
| $K_a = K_b = 10^{-5}$ | Inflection | Inflection | Inflection | Inflection |
| $K_a = K_b = 10^{-5.5}$ | Inflection | Inflection | Inflection | No inflection |
| $K_a = K_b = 10^{-6}$ | Inflection | Inflection | No inflection | No inflection |
| $K_a = K_b = 10^{-6.5}$ | Inflection | No inflection | No inflection | No inflection |
| $K_a = K_b = 10^{-7}$ | No inflection | No inflection | No inflection | No inflection |

The neutralization curve of a **mixture of two acids,** or of a **polybasic acid,** may be calculated from the data given in Chapter I, p. 32. If the titration of one acid is possible in the presence of the other, we obtain two inflection-points, the first after the neutralization of the stronger acid, and the second after the neutralization of the weaker acid. The latter case has already been discussed. Therefore, only the inflection at the first equivalence-point remains to be considered here. From equation (86), (p. 31), we find that at the first equivalence-point:

$$p_H = \tfrac{1}{2}(p_{K_1} + p_{K_2}), \quad . \; . \; . \; . \; . \quad (86)$$

$p_{K_1}$ and $p_{K_2}$ being the acid exponents of the two acids, which in this instance have the same concentration.

From the data given in § 10, Chapter I, it may be calculated that no inflection at all occurs when the first acid is no more than 100 times stronger than the second, if both acids have the same concentration. If the second acid has a concentration 100 times greater than that of the stronger acid, then the latter must have a dissociation constant which is at least 10,000 times larger than that of the weaker acid, if an inflection-point is to be observed. Such a titration does not yield accurate results, however. If the accuracy is to be at least 0.5 per cent, the first acid must have a dissociation constant which is at least 10,000 times larger than that of the second, when both acids have the same concentration. When the concentration of the weaker acid is 100 times larger than that of the stronger, then the dissociation constant of the latter must be at least $10^6$ times larger than that of the weak acid if we are to obtain satisfactory results. The authors have already discussed, in Chapter I, the fact that a dibasic acid may be considered as a mixture of two acids, the strengths of which are given by the first and second dissociation constants of the acid.

In the following table are given the ratios of $K_1$ and $K_2$ for some familiar organic acids:

| Acid | $K_1 : K_2$ | |
|---|---|---|
| Oxalic | About 1000 | Can not be titrated as a monobasic acid |
| Tartaric | About 11 | |
| Citric | About 20 | |
| Malonic | About 500 | |
| Malic | About 50 | |
| Fumaric | About 20 | |
| Maleic | About 200 | |

In all of the above instances, the ratio of $K_1 : K_2$ is so small that the acid can not be titrated as a monobasic acid. For carbonic acid:

$$K_1 = 3 \times 10^{-7}; \quad K_2 = 6 \times 10^{-11}; \quad K_1 : K_2 = 5000.$$

Hence, carbonic acid may be titrated as a monobasic acid; the accuracy, however, is not greater than 1 per cent.

In the case of phosphoric acid we have:

$$K_1 = 1.1 \times 10^{-2}; \quad K_2 = 1.95 \times 10^{-7}. \quad K_1 : K_2 = \text{about } 10^5.$$

$$K_2 = 1.95 \times 10^{-7}; \quad K_3 = 3.6 \times 10^{-13}. \quad K_2 : K_3 = \text{about } 5 \times 10^5.$$

The ratios are great enough to make it possible to titrate phosphoric acid both as a monobasic and as a dibasic acid. For a more detailed discussion the reader is referred to I. M. Kolthoff's "The Use of Indicators," p. 99.

In the following table, the authors give, by way of illustration, the data for the neutralization curve of a mixture 0.1 N with respect to both acetic and boric acids, in the neighborhood of the first equivalence-point.

Titration of a Mixture of 0.1 N Acetic Acid and 0.1 N Boric Acid
$K_1=1.8\times10^{-5}$. $K_2=6\times10^{-10}$. $K_1 : K_2=3\times10^4$

| Per Cent NaOH Equivalent to Acetic Acid | $[H^+]$ | $p_H$ | $E_{H_2}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 90 | $2 \times10^{-6}$ | 5.70 | $\varepsilon_0-5.70\times0.059=\varepsilon_0-0.336$ | |
| 95 | $9.4 \times10^{-7}$ | 6.03 | $\varepsilon_0-6.03\times0.059=\varepsilon_0-0.356$ | |
| 98 | $3.7 \times10^{-7}$ | 6.43 | $\varepsilon_0-6.43\times0.059=\varepsilon_0-0.380$ | |
| 99 | $2.3 \times10^{-7}$ | 6.64 | $\varepsilon_0-6.64\times0.059=\varepsilon_0-0.392$ | 12 |
| 100 | $1.03\times10^{-7}$ | 6.99 | $\varepsilon_0-6.99\times0.059=\varepsilon_0-0.412$ | 20 |
| 101 | $4.6 \times10^{-7}$ | 7.34 | $\varepsilon_0-7.34\times0.059=\varepsilon_0-0.432$ | 20 |
| 102 | $2.8 \times10^{-7}$ | 7.55 | $\varepsilon_0-7.55\times0.059=\varepsilon_0-0.444$ | 12 |

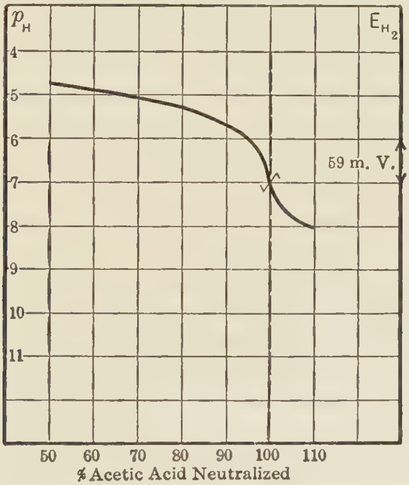

Fig. 13.—Neutralization curve, 0.1 N acetic acid in the presence of 0.1 N boric acid.

All other combinations that occur in analytical neutralizations may be reduced to the cases that have been discussed above. For details, especially regarding the titration of weak acids or bases in their salts (displacement titrations), the reader is referred to I. M. Kolthoff's "The Use of Indicators."

**6. Titration of a Complex-forming Ion.**—(*Cf.* p. 33.) If we titrate an ion, $B^+$, which forms a complex with $A^-$, according to the equation:

$$2B^+ + A^- \rightleftarrows B_2A^+,$$

we have:

$$\frac{[B^+]^2[A^-]}{[B_2A^+]} = K'_{\text{compl.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (97a)$$

Now, if we are titrating a solution of $B^+$ of concentration $c$, and have added an amount of reagent equivalent to $a$, then:

$$[B^+] = c - a,$$

$$[B_2A^+] = \tfrac{1}{2}a.$$

In order to give a rather simple formulation, it is assumed that the dissociation of the complex ion into its components is negligible in comparison with the excess of one of the ions. When the titration yields accurate results, this assumption is permissible from a practical point of view. It is assumed that the volume is constant during the titration. After the addition of an amount of reagent equivalent to $a$, we have, according to (97$a$):

$$[A^-] = \frac{[B_2A^+]}{[B^+]^2}K'_{\text{compl.}} = \frac{a}{2(c-a)^2} \times K'_{\text{compl.}}$$

At the equivalence-point we have, according to equation (97$a$):

$$[A^-] = \sqrt[3]{\frac{c}{4}K'_{\text{compl.}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (98a)$$

$$[B^+] = \sqrt[3]{2cK'_{\text{compl.}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (98a)$$

After the addition of an excess of $A^-$ equivalent to a concentration $b$, we have:

$$[A^-] = \tfrac{1}{2}b,$$

$$[B_2A^+] = \tfrac{1}{2}c,$$

$$[B^+] = \sqrt{\frac{c}{a}K'_{\text{compl.}}}$$

With the aid of these equations, we may calculate the **complex-formation curve** for the simplest reactions:

$$2B^+ + A^- \rightleftarrows B_2A^+,$$

or

$$B^+ + 2A^- \rightleftarrows BA_2^-.$$

When more ions react with each other to form a complex ion, the equations are of higher orders:

$$xB^{n+} + yA^{m-} \rightleftarrows B_xA_y^{z+} \quad \text{or} \quad B_xA_y^{z-},$$

$$\frac{[B^{n+}]^x[A^{m-}]^y}{[B_xA_y^{z\pm}]} = K'_{\text{compl.}}$$

When $[B^+]$ is known we may calculate $[A^-]$; and conversely, when $[A^-]$ is known we may calculate $[B^+]$, provided the concentration of the complex ion $[B_xA_y^{z+}]$ or $[B_xA_y^{z-}]$ is given.

In most practical instances, we encounter the complication that the neutral part, BA, is a slightly soluble substance. At the point where the precipitation begins, we can no longer apply the simple equations given above, but must also take into account the solubility product, $S_{BA}$. We obtain a new set of equations upon introducing $S_{BA}$. Another complication which we frequently meet is that not merely one complex ion is formed but often two or more:

$$Hg^{++} + 3CN^- \rightleftarrows Hg(CN)_3^-,$$

$$Hg^{++} + 4CN^- \rightleftarrows Hg(CN)_4^=.$$

In order to calculate the simple ion concentrations, we must employ equations in which the various complex constants occur. The final equation is no longer of a simple form.

It lies beyond the scope of this practical book to give a set of equations for the calculation of the simple ion concentrations in each particular instance. With the aid of the foregoing discussion, however, one should be able to calculate changes in the simple ion concentrations in any instance for which the various constants are known. On the other hand, it is possible to derive the complex constant, or the various complex constants of the system, from the practically determined data of the complex-formation curve.

*Example.*—In order to demonstrate this mode of calculation and its difficulties, we may take as an example the rather simple case of the titration of cyanide ion with silver, which is of great practical importance. The reaction is represented by the equation:[6]

$$2CN^- + Ag \rightleftarrows Ag(CN)_2^-,$$

and

$$\frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = K'_{\text{compl.}} = 10^{-21}.$$

The difficulty which we meet here is that the silver salt of the complex ion, $Ag[Ag(CN)_2]$, (usually called silver cyanide although in reality it is silver argenticyanide) is slightly soluble. Hence, we must take into consideration the equation:[7]

$$[Ag^+][Ag(CN)_2^-] = S_{Ag[Ag(CN)_2]} = 4 \times 10^{-12}.$$

When we are titrating a cyanide solution with silver nitrate, the complex ion alone will be formed until the silver-ion concentration reaches the value:

$$[Ag^+] = \frac{S}{[Ag(CN)_2^-]}.$$

At this point the precipitation of the silver-silver cyanide begins, and a further addition of silver ion does not change the concentration very much, since the concentration of the complex ion is changed but slightly by the precipitation of its silver salt.

We shall assume an original concentration of 0.1 N for the cyanide solution, and a constant volume during the titration. The concentration of the complex ion will be $5 \times 10^{-2}$ at the equivalence-point. According to equation (98*a*), $[Ag^+]$ will then be:

$$[Ag^+] = \sqrt[3]{\frac{c}{4}K'_{\text{compl.}}} = 3.0 \times 10^{-8}. \quad p_{Ag} = 7.53.$$

It follows, from the solubility product of the silver-silver cyanide, that its precipitation will begin when:

$$[Ag^+] = \frac{S}{c} = \frac{4 \times 10^{-12}}{5 \times 10^{-2}} = 8 \times 10^{-11}. \quad p_{Ag} = 10.1.$$

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[6] *Cf.* Euler, Ber. **36**, 2878 (1903); Bodländer and Eberlein, Z. anorg. Chem., **39**, 208 (1904).

[7] According to Bodländer and Lucus, Z. anorg. Chem., **41**, 192 (1904), the silver-ion concentration in a saturated silver cyanide solution is 2.2×10⁻⁶ (25°); Böttger, Z. physik. Chem., **56**, 93 (1906) found a value of 1.6×10⁻⁶, by conductivity measurement.

When the silver-ion concentration has reached this point, a further small addition of silver salt does not change the concentration of the complex ion and of [$Ag^+$] to an appreciable extent.

From the above we see that the precipitation of the silver-silver cyanide begins before the equivalence-point is reached. The jump in the potential also occurs before that point. As we shall see from the data in the table below, the titration error

TITRATION OF 0.1 N CYANIDE SOLUTION WITH SILVER NITRATE
$K'_{\text{compl.}}=10^{-21}$. $S_{AgAg(CN)_2}=4\times10^{-12}$

| Per Cent Silver Equivalent to Cyanide | [$Ag^+$] | $p_{Ag}$ | $E_{Ag}$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|---|
| 10 | $6.2\times10^{-22}$ | 21.22 | $\varepsilon_0-21.22\times0.059=\varepsilon_0-1.252$ | |
| 50 | $10^{-20}$ | 20 | $\varepsilon_0-20\times0.059=\varepsilon_0-1.180$ | |
| 80 | $10^{-19}$ | 19 | $\varepsilon_0-19\times0.059=\varepsilon_0-1.121$ | |
| 90 | $4.5\times10^{-19}$ | 18.35 | $\varepsilon_0-18.35\times0.059=\varepsilon_0-1.083$ | |
| 95 | $1.9\times10^{-18}$ | 17.72 | $\varepsilon_0-17.72\times0.059=\varepsilon_0-1.046$ | |
| 98 | $1.2\times10^{-17}$ | 16.91 | $\varepsilon_0-16.91\times0.059=\varepsilon_0-0.998$ | |
| 99 | $4.95\times10^{-17}$ | 16.31 | $\varepsilon_0-16.31\times0.059=\varepsilon_0-0.962$ | 36 |
| 99.7 | $5.5\times10^{-16}$ | 15.26 | $\varepsilon_0-15.26\times0.059=\varepsilon_0-0.900$ | 90 |
| 99.8 | $1.25\times10^{-15}$ | 14.90 | $\varepsilon_0-14.90\times0.059=\varepsilon_0-0.879$ | 210 |
| 99.9 | $5\times10^{-15}$ | 14.30 | $\varepsilon_0-14.30\times0.059=\varepsilon_0-0.844$ | 350 |
| 100 | $8\times10^{-11}$ | 10.1 | $\varepsilon_0-10.1\times0.059=\varepsilon_0-0.596$ | 2480 |
| Excess of Silver Per Cent | | | | |
| 0.1 | $8\times10^{-11}$ | 10.1 | $\varepsilon_0-10.1\times0.059=\varepsilon_0-0.596$ | 0 |
| 0.2 | $8\times10^{-11}$ | 10.1 | $\varepsilon_0-10.1\times0.059=\varepsilon_0-0.596$ | 0 |
| 1.0 | $8\times10^{-11}$ | 10.1 | $\varepsilon_0-10.1\times0.059=\varepsilon_0-0.596$ | 0 |

is so small that we may neglect it from a practical standpoint. The data in the table have been derived in the following way: We start with a 0.1 N cyanide solution, and assume that the volume does not change during the titration. The silver-ion concentration is calculated by means of the equation:

$$[Ag^+]=\frac{[Ag(CN)_2^-]}{[CN^-]^2}\cdot10^{-21}.$$

When 10 per cent of the cyanide has been titrated its concentration has become $9 \times 10^{-2}$N, whereas the concentration of the complex ion $[Ag(CN)_2^-]$ is equal to $5 \times 10^{-5}$. Hence:

$$[Ag^+] = \frac{5 \times 10^{-3}}{(9 \times 10^{-2})^2} \cdot 10^{-21} = 6.2 \times 10^{-22}. \quad p_{Ag} = 21.22.$$

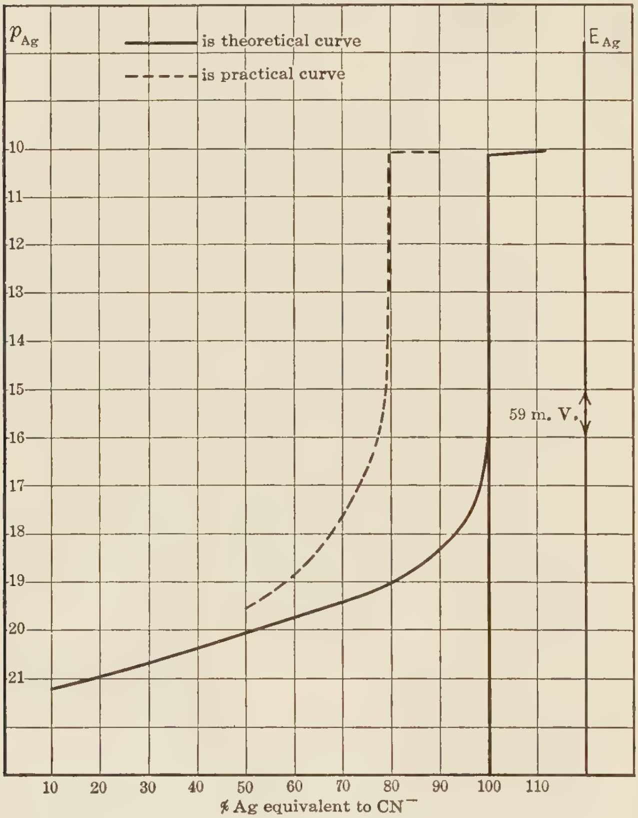

FIG. 14.—Complex-formation curve, 0.1 N cyanide and $Ag^+$.

All of the other values of $[Ag^+]$, up to the equivalence-point, have been calculated in this way.

We see that after 99.9 per cent of the equivalent amount of silver has been added, the silver-ion concentration is $5 \times 10^{-15}$. At this concentration the silver salt will not be precipitated, since $[Ag^+]$ must be in this instance at least $8 \times 10^{-11}$ before the precipitation begins. (See above.) Hence, the silver-ion concentration rises from $5 \times 10^{-15}$ to $8 \times 10^{-11}$ during the addition of the last 0.1 per cent before the equivalence-point. It is practically unchanged by a small excess of the silver salt.

The curve found by E. Müller and H. Lauterbach,[8] which is represented by the dotted curve in Fig. 14, is in good agreement with the theoretical curve. For the sake of clearness, the abscissas of the dotted curve have been shifted 2 cc. to the left in Fig. 14.

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[8] E. Müller and H. Lauterbach, Z. anorg. Chem., **121**, 178 (1922).

## CHAPTER V

## THE RELATION BETWEEN THE CHANGE IN THE RATIO OXIDANT : REDUCTANT AND THE ELECTRODE POTENTIAL IN OXIDATION-REDUCTION REACTIONS

**1. Equivalence - potential in Oxidation - reduction Reactions.**[1]—In Chapter III, p. 50, the authors discussed the equilibrium conditions in the reaction:

$$Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2. \quad . \quad . \quad . \quad (131)$$

$Ox_1$ is the oxidant which we are titrating with the reductant $Red_2$. At the equivalence-point:

$$\frac{[Ox_1]}{[Red_1]} = \frac{[Red_2]}{[Ox_2]}.$$

We also have:

$$E = \varepsilon_{0_1} + 0.0591 \log \frac{[Ox_1]}{[Red_1]} = \varepsilon_{0_2} + 0.0591 \log \frac{[Ox_2]}{[Red_2]}. \quad (133)$$

in which $\varepsilon_{0_1}$ is the normal potential of the system $Ox_1 \rightleftarrows Red_1$, and $\varepsilon_{0_2}$ that of the system $Ox_2 \rightleftarrows Red_2$.

We may calculate the equivalence-potential, $E_E$, from the last two equations:

$$\mathbf{E_E} = \frac{\varepsilon_{0_1} + \varepsilon_{0_2}}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (196)$$

When we are dealing with a reaction of the type:

$$Ox_1 + 2\,Red_2 \rightleftarrows Red_1 + 2\,Ox_2. \quad . \quad . \quad . \quad (136)$$

it follows from equations (137) to (140) that:

$$\mathbf{E_E} = \frac{2\varepsilon_{0_1} + 1\varepsilon_{0_2}}{3}. \quad . \quad . \quad . \quad . \quad . \quad (197)$$

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[1] Cf. I. M. Kolthoff, Chem. Weekblad., **16**, 408 (1919).

We shall now consider the general equation:

$$a\mathrm{Ox}_1 + b\mathrm{Red}_2 \rightleftarrows a\mathrm{Red}_1 + b\mathrm{Ox}_2,$$

whose partial-reaction potentials are:

$$\mathrm{E} = \varepsilon_{0_1} + \frac{0.059}{x} \log \left\{ \frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} \right\}^a,$$

and

$$\mathrm{E} = \varepsilon_{0_2} + \frac{0.059}{x} \log \left\{ \frac{[\mathrm{Ox}_2]}{[\mathrm{Red}_2]} \right\}^b.$$

Moreover, we know that at the equivalence-point:

$$\frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} = \frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]}.$$

Then we have:

$$\mathrm{E} = \varepsilon_{0_1} + \frac{0.059a}{x} \log \frac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} = \varepsilon_{0_2} - \frac{0.059b}{x} \log \frac{[\mathrm{Red}_2]}{[\mathrm{Ox}_2]}.$$

Or at the equivalence-point:

$$\begin{array}{rcl} b\mathrm{E} & = & b\varepsilon_{0_1} + \dfrac{0.059ab}{x} \log \dfrac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} \\ a\mathrm{E} & = & a\varepsilon_{0_2} + \dfrac{0.059ab}{x} \log \dfrac{[\mathrm{Ox}_1]}{[\mathrm{Red}_1]} \\ \hline a\mathrm{E} + b\mathrm{E} & = & b\varepsilon_{0_1} + a\varepsilon_{0_2} \end{array}$$

$$\mathrm{E_E} = \frac{b\varepsilon_{0_1} + a\varepsilon_{0_2}}{a + b}. \qquad (198)$$

*Examples.*—Reaction:

$$\mathrm{Fe^{+++} + Cu^{+} \rightleftarrows Fe^{++} + Cu^{++}}.$$

$$a = 1; \quad b = 1.$$

$$\varepsilon_{0\mathrm{Fe^{III}} \rightarrow \mathrm{Fe^{II}}} = 0.714; \quad \varepsilon_{0\mathrm{Cu^{++}} \rightarrow \mathrm{Cu^{+}}} = 0.18.$$

$$\mathrm{E_E} = \frac{.714 + .18}{2} = 0.497.$$

Reaction:

$$\mathrm{2Fe^{+++} + Sn^{++} \rightleftarrows 2Fe^{++} + Sn^{++++}}.$$

$$a = 2; \quad b = 1.$$

$$\varepsilon_{0\mathrm{FE^{III}} \rightarrow \mathrm{FE^{II}}} = 0.714; \quad \varepsilon_{0\mathrm{Sn^{IV}} \rightarrow \mathrm{SN^{II}}} = 0.138.$$

$$\mathrm{E_E} = \frac{.714 + 2 \times .138}{3} = 0.330.$$

Reaction:

$$MnO_4^- + 8H^+ + 5Fe^{++} \rightleftarrows Mn^{++} + 5Fe^{+++} + 4H_2O.$$

$$a = 1; \quad b = 5.$$

At $[H^+] = 1$,

$$\varepsilon_{0_{MNO_4 \to Mn^{++}}} = 1.52; \quad \varepsilon_{0_{Fe^{III} \to Fe^{II}}} = 0.714.$$

$$E_E = \frac{5 \times 1.52 + 0.714}{6} = 1.386.$$

**2. Change of the Electrode Potential during the Titration of an Oxidant or Reductant. Oxidation-reduction Curve.**—As we have seen from the equation which gives the relations, the electrode potential of an oxidation-reduction system is dependent only upon the ratio between the concentrations of oxidant and reductant, and not upon their total concentrations. Therefore, the change in potential *during the titration of an oxidant or reductant is independent of the total concentration of the substance to be titrated.* In the mathematical discussion of the position of the maximum value of $\frac{\Delta E}{\Delta c}$, however, we have to take the total concentrations into consideration, at least in the vicinity of the equivalence-point. We shall first consider the change of the potential in a simple case where an oxidant is titrated according to the equation:

$$Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2.$$

After the reduction of 9 per cent of the oxidant we have:

$$E = \varepsilon_0 + 0.059 \log \frac{[Ox_1]}{[Red_1]} = \varepsilon_0 + 0.059 \log \tfrac{91}{9} = \varepsilon_0 + 0.059.$$

After the reduction of half of the oxidant we have:

$$[Ox_1] = [Red_1],$$

and hence:

$$E = \varepsilon_0.$$

In this way all of the values of E may be calculated. In the neighborhood of the equivalence-point we also apply the simple equation; we neglect the amounts of $Ox_1$ and $Red_2$ that are due to the incompleteness of the reaction. If this is not permissible, as in cases where the equilibrium constant is rather large, we may calculate the corrections with the aid of equation (162). (See p. 60; *cf.* also § 3 of this Chapter, where the mathematical formulation is given.)

At the equivalence-point, as we have seen:

$$E_E = \frac{\varepsilon_{0_1} + \varepsilon_{0_2}}{2} \quad . \; . \; . \; . \; . \; . \; . \quad (196)$$

The break in the potential is dependent upon the normal potentials of the two oxidation-reduction systems that are involved. When an excess of the reductant with which we titrate has been added, the potential may be most readily calculated from the equation:

$$E = \varepsilon_{0_2} + 0.059 \log \frac{[Ox_2]}{[Red_2]}.$$

In the following table is given a summary of the above considerations.

Titration of an Oxidant. $Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2$

| Per Cent $Ox_1$ Reduced | Ratio $\frac{[Ox_1]}{[Red_1]}$ | E |
|---|---|---|
| 9 | 10 | $\varepsilon_{0_1} + 1 \times 0.059$ |
| 50 | 1 | $\varepsilon_{0_1}$ |
| 91 | 0.1 | $\varepsilon_{0_1} - 1 \times 0.059$ |
| 99 | 0.01 | $\varepsilon_{0_1} - 2 \times 0.059$ |
| 99.8 | 0.002 | $\varepsilon_{0_1} - 2.7 \times 0.059$ |
| 99.9 | 0.001 | $\varepsilon_{0_1} - 3 \times 0.059$ |
| 100 | $\sqrt{10^{\frac{\varepsilon_{0_2} - \varepsilon_{0_1}}{0.059}}}$ | $\frac{\varepsilon_{0_1} + \varepsilon_{0_2}}{2}$ |
| Excess of $Red_2$ Per Cent | Ratio $\frac{[Ox_2]}{[Red_2]}$ | |
| 0.1 | 1000 | $\varepsilon_{0_2} + 3 \times 0.059$ |
| 0.2 | 500 | $\varepsilon_{0_2} + 2.7 \times 0.059$ |
| 1 | 100 | $\varepsilon_{0_2} + 2 \times 0.059$ |

It is evident that the jump in potential depends only upon the equilibrium constant of the reaction and not upon the concentration of the solution to be titrated or of the titrating agent. In very dilute solutions, or in cases where K is moderately large, the actual concentrations also play a part in the vicinity of the equivalence-point. In the following table, the titration of a ferric iron solution with one containing cuprous copper is given as an illustration.

Titration of Ferric Iron with Cuprous Copper. $\varepsilon_{0_1}=0.714$. $\varepsilon_{0_2}=0.18$

| Per Cent Ferric Iron Reduced | $\frac{[Fe^{III}]}{[Fe^{II}]}$ | E | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|
| 9 | 10 | $0.714+0.059=0.773$ | |
| 50 | 1 | $0.714=0.714$ | |
| 91 | 0.1 | $0.714-0.059=0.655$ | |
| 99 | 0.01 | $0.714-2\times0.059=0.596$ | |
| 99.8 | 0.002 | $0.714-2.7\times0.059=0.555$ | 46 |
| 99.9 | 0.001 | $0.714-3\times0.059=0.537$ | 180 |
| 100 | 0.00003 | $0.714-4.52\times0.059=0.447$ | 900 |
| Excess of $Cu^I$ Per Cent | $\frac{[Cu^{++}]}{[Cu^{+}]}$ | | 900 |
| 0.1 | 1000 | $0.18+3\times0.059=0.357$ | |
| 0.2 | 500 | $0.18+2.7\times0.059=0.339$ | 180 |
| 1 | 100 | $0.18+2\times0.059=0.298$ | 46 |

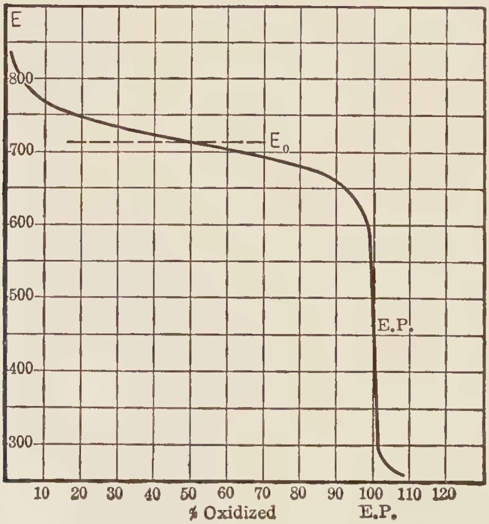

Fig. 15.—Titration of ferric iron with cuprous copper.

The maximum break in the potential occurs just at the equivalence-point. The $\frac{\Delta E}{\Delta c} - c$ curve is symmetrical on both sides of this point. This is no longer the case when the oxidant and the reductant with which we titrate react with different numbers of electrons, e.g.:

$$2Ox_1 + Red_2 \rightleftarrows 2Red_1 + Ox_2.$$

The change in potential during the titration of the oxidant is the same as that which we have calculated for the preceding table, before the equivalence-point is reached.

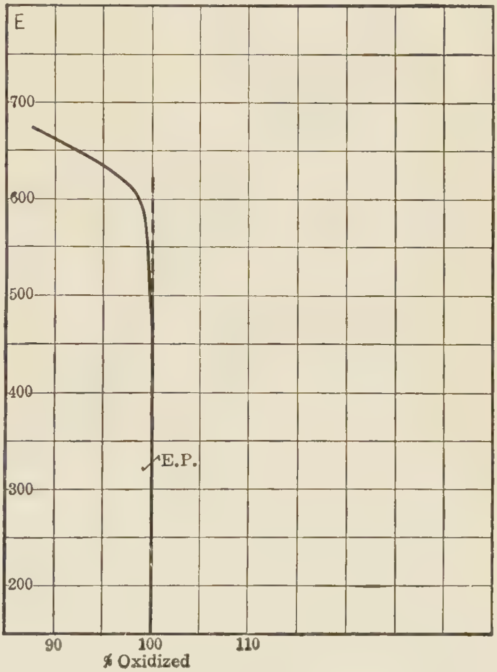

FIG. 16.—Titration of $Fe^{+++}$ with $Sn^{++}$.

At the equivalence-point:

$$E_E = \frac{2\varepsilon_{0_1} + \varepsilon_{0_2}}{3}. \quad (197)$$

When we have an excess of 0.1 per cent of reductant, expressing the ratio in equivalents, we have:

$$\frac{[Ox_2]}{[Red_2]} = 1000, \text{ and}$$

$$E = \varepsilon_{0_2} + \frac{0.059}{2} \log 1000 = \varepsilon_{0_2} + 1.5 \times 0.059.$$

In the same way we find, with 1 per cent of reductant:

$$E = \varepsilon_{0_2} + \frac{0.059}{2} \log 100 = \varepsilon_{0_2} + 0.059.$$

In the following table are given the calculated values for the titration curve of ferric iron with stannous tin.

Titration of Ferric Iron with Stannous Tin

$$2Fe^{+++} + Sn^{++} \rightleftarrows 2Fe^{++} + Sn^{++++}$$

$$2Fe^{+++} + 2e \rightleftarrows Fe^{++}. \quad E = 0.714 + \frac{0.059}{2} \log \frac{[Fe^{+++}]^2}{[Fe^{++}]^2}$$

$$Sn^{++++} + 2e \rightleftarrows Sn^{++}. \quad E = 0.138 + \frac{0.059}{2} \log \frac{[Sn^{++++}]}{[Sn^{++}]}$$

| Per Cent Ferric Iron Reduced | $\frac{[Fe^{+++}]}{[Fe^{++}]}$ | E | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|
| 50 | 1 | 0.714 = 0.714 | |
| 91 | 0.1 | 0.714 − 1 × 0.059 = 0.655 | |
| 99 | 0.01 | 0.714 − 2 × 0.059 = 0.596 | 46 |
| 99.8 | 0.002 | 0 714 − 2.7 × 0.059 = 0.555 | 180 |
| 99.9 | 0.001 | 0.714 − 3 × 0.059 = 0.537 | 2070 |
| 100 | $3.2 \times 10^{-7}$ | 0.714 − 6.5 × 0.059 = 0.330 | 1030 |
| Excess of Stannous Ion Per Cent | $\frac{[Sn^{++++}]}{[Sn^{++}]}$ | | |
| 0.1 | 1000 | 0.138 + 1.5 × 0.059 = 0.2265 | 90 |
| 0.2 | 500 | 0.138 + 1.35 × 0.059 = 0.2175 | 23 |
| 1 | 100 | 0.138 + 1 × 0.059 = 0.197 | |

When we have more complicated systems, as for instance, when we are using permanganate, dichromate, or iodate, as oxidants in acid solution, we may apply the more complicated equations which were derived in Chapter III (pp. 64 and 65).

As an example we may consider the titration curve of ferrous iron with permanganate in a solution whose hydrogen-ion concentration is 1 N at the equivalence-point. Before the equivalence-point is reached we have the ferrous-ferric potential. When 99 per cent of the iron is oxidized:

$$\frac{[Fe^{+++}]}{[Fe^{++}]} = 100,$$

and

$$E = \varepsilon_{0_{Fe^{III} \rightarrow Fe^{II}}} + 0.059 \log 100 = \varepsilon_0 + 2 \times 0.059.$$

At the equivalence-point we have:

$$E_E = \frac{b\varepsilon_{0_1} + a\varepsilon_{0_2}}{a+b} = \frac{5\varepsilon_{0_{MnO_4}} + \varepsilon_{0_{Fe}}}{6} \text{ (p. 107)}. \quad . \quad . \quad (198)$$

With an excess of 0.1 per cent permanganate, the ratio

$$[MnO_4^-] : [Mn^{++}] = 0.001,$$

and

$$E = \varepsilon_{0_{MnO_4}} + \frac{0.059}{5}\log\frac{[MnO_4^-]}{[Mn^{++}]}$$

$$= \varepsilon_{0_{MnO_4}} - \frac{3 \times 0.059}{5}([H^+] = 1).$$

The values in the following table were calculated in this way.

TITRATION OF FERROUS IRON WITH PERMANGANATE. $[H^+]=1$

$$MnO_4^- + 8H^+ + 5Fe^{++} \rightleftarrows Mn^{++} + 5Fe^{+++} + 4H_2O$$

$$5Fe^{+++} + 5e \rightleftarrows 5Fe^{++}. \qquad E = 0.714 + \frac{0.059}{5}\log\frac{[Fe^{+++}]^5}{[Fe^{++}]^5}$$

$$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O. \qquad E = 1.52 + \frac{0.059}{5}\log\frac{[MnO_4^-]}{[Mn^{++}]}$$

| Per Cent Ferrous Iron Oxidized | $\frac{Fe^{lc}}{Fe^{\circ}}$ | E | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|---|
| 91 | 10 | $0.714 + 1 \times 0.059 = 0.773$ | |
| 99 | 100 | $0.714 + 2 \times 0.059 = 0.832$ | |
| 99.8 | 500 | $0.714 + 2.7 \times 0.059 = 0.873$ | 46 |
| 99.9 | 1000 | $0.714 + 3 \times 0.059 = 0.891$ | 180 |
| 100 | $4 \times 10^{-12}$ | $0.714 + 11.4 \times 0.059 = 1.386$ | 4950 |
| Excess of Permanganate Per Cent | $\frac{[MnO_4^-]}{[Mn^{++}]}$ | | 990 |
| 0.1 | 0.001 | $1.52 - \frac{3}{5} \times 0.059 = 1.485$ | 30 |
| 0.2 | 0.002 | $1.52 - \frac{2.7}{5} \times 0.059 = 1.488$ | 10 |
| 1 | 0.01 | $1.52 - \frac{2}{5} \times 0.059 = 1.496$ | |

The curve that corresponds to the data of the foregoing table is given in Fig. 17. The dotted curve corresponds to the values that were found by experiment. It has been shifted two abscissa units to the right in the figure. The agreement between the two curves is very good.

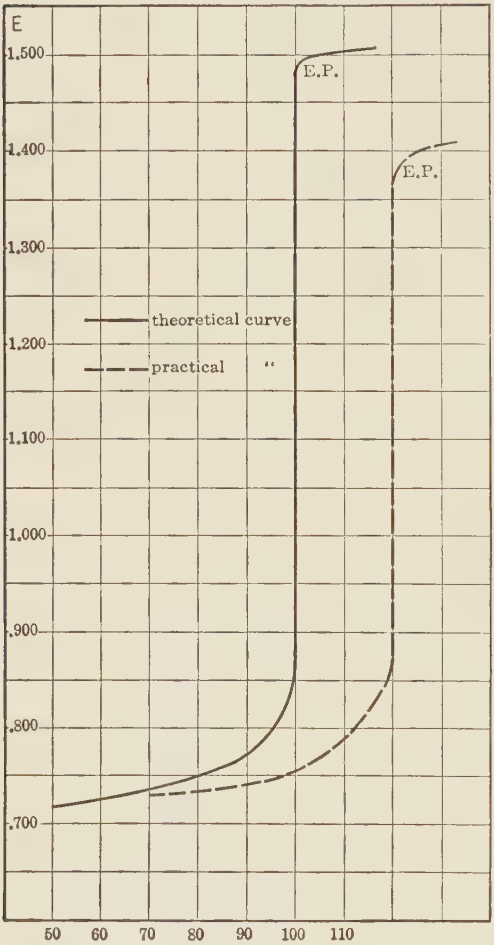

Fig. 17.—Titration of ferrous iron with permanganate.

In Fig. 18 are given curves corresponding to the $\frac{\Delta E}{\Delta c}-c$ plots for the three cases discussed above. These curves illustrate fully the differences in the nature of the change in $\frac{\Delta E}{\Delta c}$ values in these three instances.

**3. Titration of a Mixture of Different Oxidants or Reductants.**—This case may be reduced to the general one which was discussed in the preceding paragraph. In order to decide whether we can titrate one reductant in the presence of another, we have to consider the problem of the titration of the stronger reductant with the oxidized form of the other reductant. If we have, for example, a mixture of cuprous and ferrous ions, the cuprous ion is the stronger reductant. In the titration with a strong oxidant, e.g., permanganate, the cuprous ion is oxidized first. At the first equivalence-point, when practically all of the copper is oxidized, we have the equilibrium:

$$Cu^{++} + Fe^{++} \rightleftarrows Cu^{+} + Fe^{+++},$$

in which the various reactants have the same concentration ratios as at the equivalence-point of the titration of cuprous ion with ferric.

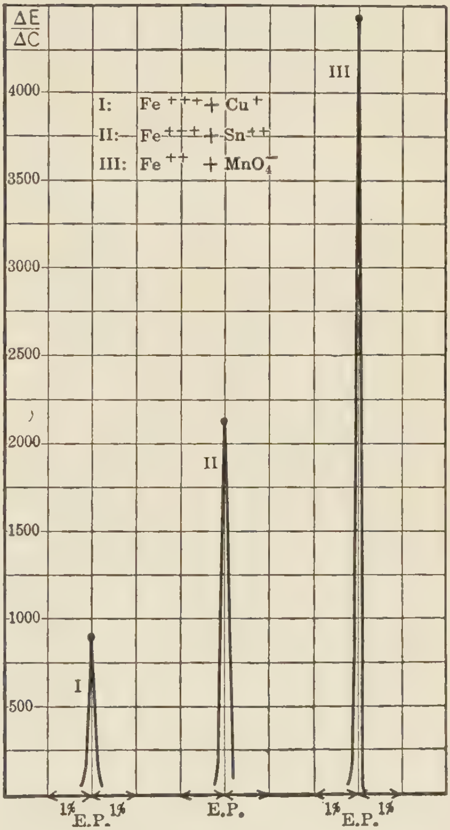

FIG. 18.—Maxima of $\frac{\Delta E}{\Delta c} \sim c$ curves at equivalence-points of oxidation-reduction titrations.

Therefore, the magnitude of the break in potential, i.e., the sharpness of the titration, is dependent only upon the difference between the normal potentials of the components that are present in the solution. The potential at the first equivalence-point may be calculated according to the equation derived in § 1 of this Chapter.

**4. Mathematical Formulation of the Variation in $\frac{\Delta E}{\Delta c}$.**—We shall start again with the simple reaction:

$$Ox_1 + Red_2 \rightleftarrows Red_1 + Ox_2.$$

This can be made clearer by means of a practical example, as:

$$Fe^{+++} + Cu^{+} \rightleftarrows Fe^{++} + Cu^{++}.$$

The original concentration of the cuprous ion is equal to $c$. We now add an amount of ferric solution equivalent to a concentration $y$. If the concentration of cuprous ion is then equal to $x$, an amount $(c - x)$ of $Cu^+$ has been transformed into cupric ion; hence:

$$[Cu^{++}] = c - x,$$

also

$$[Fe^{++}] = c - x.$$

From this we have:

$$[Fe^{+++}] = y - (c - x).$$

The application of the law of mass action gives:

$$\frac{(y - c + x)x}{(c - x)^2} = K.$$

The potential of the electrode during the titration is:

$$E = \varepsilon_{0_{Fe^{III} \rightarrow Fe^{II}}} - A \log \frac{y - c + x}{c - x};$$

(Here A is 0.0591 at 25° C., *cf.* p. 80.)
By differentiation we obtain:

$$\frac{dx}{dy} = -\frac{x(c - x)}{c(y - c) + x(y + c)},$$

$$\frac{dE}{dy} = \frac{Ac}{c(y - c) + x(y + c)}.$$

At the point where $\frac{dE}{dy}$ is a maximum, we have:

$$\frac{d}{dy}\{c(y - c) + x(y + c)\} = 0,$$

or

$$\frac{d}{dx}\{c(y - c) + x(y + c)\}\frac{dx}{dy} = 0.$$

$$\frac{d}{dx}\{c(y - c) + x(y + c)\} = (c + x)\{c(y - c) + x(y + c)\}$$
$$- x(y + c)(c - x) = 0.$$

$$c(y - c)(c + x) = -2x^2(y + c).$$

From the last equation we see that the maximum value of $\frac{dE}{dy}$ is not exactly at the equivalence-point. At this point $y$ is equal to $c$, and the left-hand member of the equation becomes zero, whereas the right-hand member has a finite value. Hence the theoretical maximum occurs before the equivalence-point. In cases where the titration is practicable, i.e., when K is sufficiently large, the difference is so small that it can hardly be estimated.

$$y - c = -\frac{4x^2c}{c(c + x) + 2x^2},$$

$$c - y \textit{ is positive.}$$

At the equivalence-point, $y = c$.

$$\frac{x^2}{(c - x)^2} = \mathrm{K}.$$

$$x_e = \frac{c\sqrt{\mathrm{K}}}{1 + \sqrt{\mathrm{K}}},$$

and

$$\frac{dE}{dy} = \frac{\mathrm{A}c}{c(y - c) + x(y + c)} = \frac{\mathrm{A}}{2x_e} = \frac{\mathrm{A}}{2}\cdot\frac{1 + \sqrt{\mathrm{K}}}{c\sqrt{\mathrm{K}}}.$$

By approximation it is possible to find a value of $x$ that is very close to the value at the maximum.

We found above:

$$c - y = \frac{4x^2c}{c(c + x)},$$

which is approximately equal to $\frac{4x^2}{c}$.

Then we have:

$$(y - c + x)x = \mathrm{K}(c - x)^2 = \mathrm{K}c^2,$$

or

$$x = c\sqrt{\mathrm{K}}.$$

At this point, it is necessary to lay stress on the fact that this value of $x$ differs but slightly from that of $x$ at the equivalence-point. Their ratio is only $1 + \sqrt{\mathrm{K}}$; our approximations, however, are only of the same order. We may calculate the exact values of $y$ and $\frac{dE}{dy}$ at $x = c\sqrt{\mathrm{K}}$ in order to control the correctness of the equations, and to see whether $\frac{dE}{dy}$ is larger than at the equivalence-point.

At $x = c\sqrt{K}$, we have:

$$y = c(1 - 2K + K\sqrt{K}).$$

Then we have:

$$\frac{dE}{dy} = \frac{Ac}{c(-2Kc + Kc\sqrt{K}) + c\sqrt{K}\,\{c(2 - 2\sqrt{K}) + cK\sqrt{K}\}}$$

$$= \frac{A}{c\sqrt{K}} \cdot \frac{1}{2 + K + K\sqrt{K} - 4\sqrt{K}}$$

$$= \frac{A}{2c\sqrt{K}} \cdot \frac{1}{1 - 2\sqrt{K} + \dfrac{K + K\sqrt{K}}{2}}.$$

This value is larger than $\frac{dE}{dy}$ at the equivalence-point when it is equal to:

$$\frac{A}{2c\sqrt{K}}(1 + \sqrt{K}).$$

The difference is actually so small that it will not be observed.

In order to get an idea of how $x$ changes with $y$, we may introduce as $x$-concentration a factor which expresses how much larger or smaller the concentration is than at the equivalence-point. The equivalence-concentration is given by:

$$\frac{x^2}{(c - x)^2} = K; \quad \frac{x}{c - x} = \sqrt{K},$$

$$x_e = \frac{c\sqrt{K}}{1 + \sqrt{K}}.$$

If we now let $x = \alpha x_e$, we have:

$$\frac{\left(y - c + \dfrac{\alpha c\sqrt{K}}{1 + \sqrt{K}}\right)\dfrac{\alpha c\sqrt{K}}{1 + \sqrt{K}}}{\left(c - \dfrac{\alpha c\sqrt{K}}{1 + \sqrt{K}}\right)^2} = K,$$

or

$$y = c\frac{\mathrm{K}+\mathrm{K}^2+2\mathrm{K}\sqrt{\mathrm{K}}+\alpha(\sqrt{\mathrm{K}}+\mathrm{K}-2\mathrm{K}\sqrt{\mathrm{K}}-2\mathrm{K}^2)+\alpha^2(\mathrm{K}^2-\mathrm{K})}{\alpha\sqrt{\mathrm{K}}(1+\sqrt{\mathrm{K}})}$$

Now, if $\alpha$ is larger than 1 (i.e., if the equivalence-point has not been reached) we have as a rough approximation (when K is smaller than $10^{-10}$):

$$y = c\frac{\alpha(\sqrt{\mathrm{K}}+\mathrm{K}) - \alpha^2\mathrm{K}}{\alpha\sqrt{\mathrm{K}}(1+\sqrt{\mathrm{K}})} = c(1 - \alpha\sqrt{\mathrm{K}}),$$

and when $\alpha < 1$,

$$y = c\left(1 + \frac{1}{\alpha}\sqrt{\mathrm{K}}\right).$$

From the above we have, when $\mathrm{K} < 10^{-10}$:

$$\begin{array}{ll}
x = x_e & y = c \\
x = 10x_e & y = c(1 - 10^{-4}) \\
x = 100x_e & y = c(1 - 10^{-3}) \\
x = 0.1x_e & y = c(1 + 10^{-4}) \\
x = .01x_e & y = c(1 + 10^{-3})
\end{array}$$

From the foregoing it is evident that even in the simple case in which we are dealing with the reaction:

$$\mathrm{Ox}_1 + \mathrm{Red}_2 \rightleftarrows \mathrm{Red}_1 + \mathrm{Ox}_2,$$

we get equations which are impracticable and difficult to solve.

The situation is much more complicated when we attempt to discuss the general equation:

$$a\ \mathrm{Ox}_1 + b\ \mathrm{Red}_2 \rightleftarrows a\ \mathrm{Red}_1 + b\ \mathrm{Ox}_2.$$

If we consider the reaction:

$$\mathrm{MnO_4^-} + 8\mathrm{H^+} + 5\mathrm{Fe^{++}} \rightleftarrows \mathrm{Mn^{++}} + 5\mathrm{Fe^{+++}} + 4\mathrm{H_2O},$$

we have:

$$\frac{[\mathrm{MnO_4^-}][\mathrm{Fe^{++}}]^5}{[\mathrm{Mn^{++}}][\mathrm{Fe^{+++}}]^5} = 10^{-68.6}. \quad (\text{At } [\mathrm{H^+}] = 1).$$

If the original concentration of ferrous iron is $c$, and if we add an amount of permanganate equivalent to $y$, we may derive the relation:

$$\frac{dE}{dy} = \frac{5Ac}{5c(y - c) + x(5c + y)},$$

and the maximum is found when:

$$\frac{d}{dy}\{5c(y - c) + x(5c + y)\} = 0.$$

Or:

$$y - c = -\frac{6cx(4c + 2x)}{25c^2 + 9cx + 2x^2} = -\frac{12cx(2c + x)}{25c^2 + 9cx + 2x^2}.$$

At the equivalence-point, $y = c$; therefore we see that the maximum is again located just before the equivalence-point, where $c - y$ is positive.

The mathematical equations will not be discussed in detail, as they are not practicable. In special instances it is better to calculate values of $x$ that correspond to those of $c$ and $y$, by means of the value of the equilibrium constant, and to plot these values in a curve, from which the maximum value of $\frac{\Delta E}{\Delta y}$ may be derived.

## CHAPTER VI

# GENERAL CONDITIONS FOR THE PERFORMANCE OF POTENTIOMETRIC TITRATIONS

**1. General Conditions which Apply to All Titrations.**—Chemical reactions must fulfill the following conditions if they are to be considered satisfactory to serve as the foundations of titration methods:

*First:* The reaction must proceed in only one manner, i.e., other reactions than the one indicated by the equation must not occur. These other (" side ") reactions are often found in the case of organic substances. A well-known example in the inorganic field is the oxidation of hydrazine, which may yield various oxidation products. Titrations of this kind only yield good results if we find the conditions under which the reaction proceeds entirely according to some special equation.

If the reaction scheme is not a simple one, and if several reaction products are formed, as is the case, for example, in the oxidation of sugars with alkaline copper solution, the method may no longer be classed as one of the refined titrations of volumetric analysis. Empirical tables must be used in place of stoichiometrical equations, and it is always doubtful to what extent foreign substances will affect the result.

*Second:* The reaction must be a stoichiometric one. When multivalent ions unite to form a precipitate, it often happens that the precipitate is not of uniform composition, but consists of a mixture of salts of different compositions. This is especially true with ferrocyanide as a reagent for heavy metals. We shall find that the precipitate contains the alkali metal, in a variable ratio to the amount of the heavy metal. (*Cf.* Part II, p. 270.)

It often happens, moreover, that simple precipitates are not entirely pure, but include an excess of one of the constituent ions, thus causing an error in the determination. In analytical chemistry this error is usually attributed to "adsorption." The authors wish to remark that the word "adsorption," when so used, is a generic term for a number of phenomena, as, for example: mechanical inclusion; chemical adsorption (silver halides); physical adsorption; mix-crystal formation, etc. In a systematic study of the errors of titrations, it is necessary to make a special study in each case, in order to determine the cause of the error.

*Third:* The velocity with which the state of equilibrium is reached must be sufficiently great. When the reaction velocity is very small the reaction can not be the basis of a practical titration. In many oxidation-reduction reactions, heating the solution has a favorable effect (undoubtedly because the opposed reaction velocities are increased, thus hastening the attainment of equilibrium); the addition of catalysts may also have a favorable influence. In some instances the addition of an excess of reagent, and back-titration of the excess will yield good results.

*Fourth:* The reaction must proceed as completely as possible in one direction, i.e., the equilibrium constant must be very small. In Chapters I to V this question was discussed *in extenso*. In instances where a slightly soluble substance is formed, the solubility of which is too large for a direct titration, the addition of an excess of the precipitating ion, followed by filtration, and back-titration with a suitable reagent, will yield satisfactory results. Many organic anions may be determined in this manner. With the aid of the equations given in Chapter I, we may determine the solubility in the presence of excess of one of the ions, and hence we may calculate the error that is due to solubility.

*Fifth:* We must have an indicator for the detection of the position of the equivalence-point. In potentiometric titrations we do not add a foreign substance as indicator, since the change in the electrode potential (indicator electrode) tells us when an equivalent amount of reagent has been added (*cf.* Chapters IV and V).

**2. Special Considerations for the Performance of Potentiometric Titrations.**—In the preceding paragraph, the term

**indicator electrode** has been used to designate the electrode whose change in potential is measured during the titration. This is the term used by Erich Müller. Now, if we are dealing with direct combinations of ions, in which one or more cations, B, react with an anion, A, the concentration of the B-ions, as well as that of the A-ions, is changing rapidly in the neighborhood of the equivalence-point, as we have seen in the preceding section. In general, it is immaterial in these cases whether we use an electrode that changes as the B-ion concentration changes, or one that responds to changes of A-ion concentration.

Let us consider, for example, the reaction:

$$Ag^+ + I^- \rightleftarrows AgI.$$

We may use an iodine electrode as indicator, as well as one of metallic silver. An iodine electrode may be prepared by bringing a bright platinum wire or foil into contact with a little iodine.

The potential of the silver electrode changes according to the relation:

$$Ag \rightleftarrows Ag^+ + e; \quad E_{Ag} = \varepsilon_{0Ag} - 0.059 p_{Ag}.$$

The potential of the iodine electrode, according to:

$$I_2 + 2e \rightleftarrows 2I^-; \quad E_{I_2} = \varepsilon_{0I_2} + \frac{0.059}{2}. \quad 2p_{I^-} = \varepsilon_{0I_2} + 0.059 p_{I^-}$$

(The solution must be saturated with iodine).

We may write $\frac{S_{AgI}}{[Ag^+]}$ instead of $[I^-]$, where $S_{AgI}$ is a constant, (solubility product of silver iodide). Hence the potential of the iodine electrode is:

$$E_{I_2} = \varepsilon_0' - 0.059 p_{Ag}.$$

The potential of the iodine electrode, therefore, changes in exactly the same way with changing silver-ion concentration as the silver electrode. In fact, I. M. Kolthoff [1] has shown that the iodine electrode may be used for the measurement of the concentrations of ions of metals that form slightly soluble iodides (silver, mercury; *cf.* p. 196). In the case of the titration of silver with iodide, we get the same jump in potential with either a silver or an iodine electrode.

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[1] I. M. Kolthoff, Rec. trav. chim., **41**, 174 (1922).

It is not always immaterial whether we use an electrode of B or A, however. As an illustration, let us consider the reaction:

$$4\mathrm{Ag}^+ + \mathrm{Feoc} \rightleftarrows \mathrm{Ag_4Feoc}\,^{2}.$$

The potential of the silver electrode changes according to the equation:

$$\mathrm{E_{Ag}} = \varepsilon_{0\mathrm{Ag}} - 0.059 p_{\mathrm{Ag}}.$$

We obtain a ferrocyanide electrode by making an oxidation-reduction electrode with the addition of a little ferricyanide:

$$\mathrm{E} = \varepsilon_0 + 0.059 \log \frac{[\mathrm{Feic}]}{[\mathrm{Feoc}]}.$$

If we keep the [Feic] constant, we may write for the electrode potential:

$$\mathrm{E_{Feoc}} = \varepsilon_0' + 0.059 p_{\mathrm{Feoc}},$$

where $p_{\mathrm{Feoc}}$ is the ferrocyanide exponent.

In this case we may write $\frac{\mathrm{S_{Ag_4Feoc}}}{[\mathrm{Ag}^+]^4}$ in place of [Feoc], and we have:

$$\mathrm{E_{Feoc}} = \varepsilon_0'' - 4 \times 0.059 p_{\mathrm{Ag}}.$$

From this we see that the ferrocyanide electrode changes its potential four times as much as the silver electrode for a given change in silver-ion concentration. If there were no complications, the jump in potential would be four times as great with the ferrocyanide electrode as with the silver.

In neutralization reactions the indicator electrode for hydrogen ions is, at the same time, an indicator for hydroxyl ions,

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[2] In agreement with Erich Müller, the authors will use the abbreviation Feoc for $\mathrm{Fe(CN)_6^{\equiv}}$, and Feic for ferricyanide ion.

because the equilibrium between the two ions is governed by the relation:

$$[H^+][OH^-] = Kw.$$

Hence an electrode that indicates hydrogen ions changes its potential in the same way as one that indicates hydroxyl ions.

Each partial reaction in an oxidation-reduction titration is an oxidation-reduction system; we are restricted to the use of an unattackable metal—usually bright platinum—for both systems.

**3. Irreversibility of One of the Partial Reactions.**—As we have seen in the preceding paragraph, from a theoretical standpoint we may use a special indicator electrode for each partial reaction. Practically, however, we are restricted in our choice both of anion and cation electrode. When we titrate cations that stand above hydrogen in the electromotive force series, the corresponding metal electrode is usually irreversible, owing to evolution of hydrogen, polarization, oxidation, or passivation. The irreversibility is especially noticeable when the corresponding ion concentrations become very small. A zinc or cadmium electrode, for example, may be used for the measurement of higher concentrations of zinc or cadmium ion; these electrodes are impracticable for potentiometric titrations, however, since they become oxygen electrodes at small ion concentrations, and the jump in potential is in a direction opposite to that which we should expect.[3]

Dutoit has suggested an improvement upon the use of the metallic electrodes. He uses an auxiliary platinum anode and, as cathode, a bright platinum foil which is polarized cathodically during the titration, so that a fresh metal surface is continually formed. This method will be discussed later (p. 152).

A lead electrode does not give reproducible values at very small lead-ion concentrations. Therefore, if we wish to titrate lead with ferrocyanide, we can not use a lead electrode, but must employ a ferrocyanide electrode. The latter may be prepared as described in §2, by adding a little ferricyanide to the solution, and taking bright platinum as the electrode material. Its potential is governed by the equation:

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[3] *Cf.*, for example, Hedrich, Dissertation, Dresden (1919); Erich Müller, Die Elektrometrische Massanalyse, 2d Ed. (1923), p. 44.

$$E = \varepsilon_0 + 0.059 \log \frac{[\text{Feic}]}{[\text{Feoc}]}.$$

In the titration of lead with ferrocyanide, we have the reaction:

$$2\text{Pb}^{++} + \text{Feoc}^{\equiv} \rightleftarrows \text{Pb}_2\text{Feoc},$$

and

$$[\text{Feoc}^{\equiv}] = \frac{S_{\text{Pb}_2\text{Feoc}}}{[\text{Pb}^{++}]^2}.$$

Upon introducing this value, and taking [Feic] as a constant, we have:

$$F_{\text{Feoc}} = \varepsilon_0' - 0.059 \times 2p_{\text{Pb}}.$$

Therefore, the ferrocyanide electrode responds to the concentration of lead ions. This is of great practical importance. If we have a mixture of ferricyanide and lead ferrocyanide in contact with platinum, the system behaves both as a lead and as a ferrocyanide electrode.

Let us consider the case of the titration of a lead salt with sulphate, or the reverse. There is no satisfactory electrode for sulphate ions, nor can we use the lead electrode. The ferricyanide-lead ferrocyanide electrode is useful in this instance, because it changes its potential with the variations of the lead-ion concentration. As far as the authors are aware, this principle has never been used for the determination of sulphate.[4]

The authors desire to suggest that electrodes of the type discussed above open a wide field of application in potentiometric titrations, for those instances in which we have no direct electrode for either partial reaction. The Feic-$\text{Pb}_2$Feoc electrode, for example, might be useful in the titration of lead with chromate, carbonate, etc., provided the reaction of lead with these anions occurs without side-reactions. It might also be possible to use a ferricyanide-zinc ferrocyanide electrode as an indicator for zinc ions, etc. Or an iodine-silver iodide electrode may be used for silver ions. Kolthoff proved (1922) that $Cl^-$ could be titrated with silver nitrate with the $I_2$-AgI electrode.

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[4] A preliminary investigation, made by Kolthoff, and hitherto unpublished, proved that this method yields excellent results. In aqueous solutions it takes a long time for the equilibrium to become established; in the presence of alcohol a satisfactory determination may be made in a few minutes' time.

Turning our attention once more to the Feic-$Pb_2$Feoc electrode, we find that we may have three different cases in titrations:

*a.* The solubility of the lead salt which is formed is much greater than that of lead ferrocyanide. Obviously, the solubility must not be too great, or there would be no jump in potential. (*Cf.* Chapters I and IV.)

Now, if we titrate the lead salt with an anion such that the solubility of the salt which is formed is much greater than that of lead ferrocyanide, the break in potential at the equivalence-point corresponds exactly to that which we find by calculation from the solubility product of the slightly soluble lead salt, and the electrode behaves as a lead electrode (with the additional advantage that its potential changes four times as rapidly, with the lead-ion exponent, as does that of the lead electrode).

*b.* The solubility of the lead salt which is formed is of the same order as that of lead ferrocyanide. In this case the lead salt PbA will be precipitated until the equivalence-point is reached. An excess of the anion $A^=$ will depress the solubility but it may also react with the lead ferrocyanide:

$$2A^= + Pb_2Feoc \rightleftarrows 2PbA + Feoc^{\equiv}.$$

As long as PbA and $Pb_2$Feoc are present as insoluble compounds, we have:

$$[Pb^{++}][A^=] = S_{PbA}; \quad [Pb^{++}] = \frac{S_{PbA}}{A^=}$$

$$[Pb^{++}]^2[Feoc^{\equiv}] = S_{Pb_2Feoc}; \quad [Pb^{++}]\sqrt{\frac{S_{Pb_2Feoc}}{Feoc^{\equiv}}}.$$

From which we have:

$$\frac{S^2_{PbA}}{S_{Pb_2Feoc}} = \frac{[A^=]^2}{[Feoc^{\equiv}]}.$$

We can calculate from this ratio how much of the excess of $A^{=}$ is transformed into PbA, and how large $[\text{Feoc}^{\overset{=}{=}}]$ will be. We can also calculate the jump in potential that will occur when the equivalence-point is passed. This break in potential will be of the same order as in the titration of lead with ferrocyanide, when both lead salts, PbA and $Pb_2Feoc$, have solubilities of the same order.

*c.* The solubility of the lead salt formed is much smaller than that of $Pb_2Feoc$. In the titration of a lead solution with $A^{=}$, PbA will be first precipitated up to the equivalence-point. An excess of $A^{=}$ will react with the $Pb_2Feoc$ until equilibrium prevails, as we have seen in section *b*, above. But the conditions are now such that $[A^{=}]$ will remain very small as long as solid $Pb_2Feoc$ is present. The term $\frac{S^2_{PbA}}{S_{Pb_2Feoc}}$, in the equation derived above, is very small, because the solubility of PbA is so small compared with that of $Pb_2Feoc$. Hence, after the equivalence-point has been reached, an excess of $A^{=}$ will react almost quantitatively according to:

$$Pb_2Feoc + 2A^{=} \rightarrow 2PbA + \text{Feoc}^{\overset{=}{=}}.$$

When all of the $Pb_2Feoc$ has reacted in this way we have a second jump in the potential, the magnitude of which is only dependent upon the solubility product, $S_{Pb_2Feoc}$.

Hence, when we titrate a lead salt with an anion which forms the salt PbA, the solubility of which is much less than that of $Pb_2Feoc$, we observe two breaks in the potential. The first corresponds to the point where all of the lead is transformed into PbA; this is the real end-point in the present instance. The second break corresponds to the point where all of the lead ferrocyanide is transformed into PbA. The amount of reagent needed between the two potential jumps is equivalent to the amount of lead ferrocyanide present.

If we are carrying out the reverse titration, that of a solution of $A^{=}$ with a lead solution, under the conditions mentioned, the excess of $A^{=}$ that is present in the solution at the beginning of the titration will react with the $Pb_2Feoc$, to form an amount of $\mathrm{Feoc}^{----}$ equivalent to the quantity of $\mathrm{Pb_2Feoc}$ added. After the first break in potential has been reached, a further addition of lead salt causes the formation of $\mathrm{Pb_2Feoc}$. When this has taken place quantitatively, a second jump in the potential occurs, which corresponds to the end-point of the titration. In the latter case it is more practical to use a little of a highly soluble ferrocyanide, as $\mathrm{K_4Feoc}$, rather than lead ferrocyanide, in the construction of the electrode. Under these conditions, the first break in potential corresponds to the end-point of the titration.

In many oxidation-reduction reactions, the electrode is not reversible for one of the partial reactions. This is the case, for example, in the titration of sodium thiosulphate, or sulphite, with iodine:

$$\mathrm{SO_3^{=}} + \mathrm{I_2} + \mathrm{H_2O} \rightleftarrows \mathrm{SO_4^{=}} + 2\mathrm{H^+} + 2\mathrm{I^-}.$$

With the partial reactions:

$$\mathrm{SO_3^{=}} + \mathrm{H_2O} \rightleftarrows \mathrm{SO_4^{=}} + 2\mathrm{H^+} + 2e,$$

and

$$\mathrm{I_2} + 2e \rightleftarrows 2\mathrm{I^-}.$$

The sulphite-sulphate electrode is not reversible. The same is true of the thiosulphate-tetrathionate electrode. It is not yet clear why these electrodes are not reversible; probably the reactions that are represented by the equations do not take place directly, but by way of intermediate steps.

Nevertheless, reactions of this sort may be used for potentiometric titrations if one of the partial reactions is reversible, which is true of the iodine electrode in the present example. It is not possible, however, to calculate the jump in potential in the vicinity of the equivalence-point. It must be decided empirically whether such a titration is possible or not.

Sometimes the platinum electrode is not affected at all by a reductant. It then behaves more or less like an oxygen electrode. We meet this case in the titration of an oxalate with permanganate in acid solution. The potential does not change to an appreciable extent before the equivalence-point is reached.

In this case it is not possible to calculate the equivalence-potential, $E_E$; it can only be determined in an empirical way.

Finally, it should be noted here that many oxidation-reduction reactions do not take place exactly according to the equations that are given for them. For example:

$$Cr_2O_7^{=} + 14H^+ + 6e \rightleftarrows 2Cr^{+++} + 7H_2O.$$

According to the equation, the potential of the chromic acid-trivalent chromium electrode is:

$$E = \varepsilon_0 + \frac{0.059}{6} \log \frac{[Cr_2O_7^{=}][H^+]^{14}}{[Cr^{+++}]^2}.$$

In fact, however, the chromic-ion concentration has but little, if any, influence on the potential of this electrode.

The same holds true for the permanganate potential:

$$E = \varepsilon_0 + \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{++}]}.$$

This equation does not express the real conditions, because of the reaction between permanganate and manganous ions.

We must therefore be cautious in the application of theoretical considerations in cases where the electrode reactions are not quite reversible. The experimental results must then be the basis of the decision as to whether the titration is possible or not.

# PART II

# PRACTICAL APPLICATIONS

## A.—GENERAL CONSIDERATIONS

## CHAPTER VII

## THE TECHNIQUE OF POTENTIOMETRIC TITRATIONS

**1. Outline of the Potentiometric Method.**—We have no reliable and simple means of measuring a single potential difference. We may, however, determine the potential of an electrode by means of another electrode which has a constant potential (a so-called standard half-cell). By connecting the two electrodes we may build up a cell, or element, the electromotive force (E.M.F.) of which we are able to measure. The change in the E.M.F. during a potentiometric titration is exactly equal to the change of the potential of the indicator electrode, because the reference electrode has a constant potential.

The method that is usually employed in the measurement of the electromotive force of a cell is the Poggendorf-Du Bois-Raymond method, or, in other words, the potentiometer method. In principle it consists in balancing the potential difference that is to be measured against a known opposed potential difference. When the unknown is balanced in this manner, no current can flow from it through a current-indicating instrument such as a galvanometer.

The principle may be illustrated by the arrangement shown in Fig. 19. S is a battery having an E.M.F. greater than that of the unknown cell, X, the E.M.F. of which is to be determined. A common accumulator is generally very suitable as a source of current, S. SA and SB are thick copper of negligible resistance. AB is a slide wire of strictly uniform cross-section throughout its length (a wire of the kind which is used, for example, in measurements of electrical conductance). Hence, there is a uniform fall of potential from A to B.

The contact, C, which slides along the wire AB, is so connected to the unknown element, X, that the positive pole of the battery corresponds to the positive pole of X. The negative pole of X is connected to B, the negative pole of the battery.

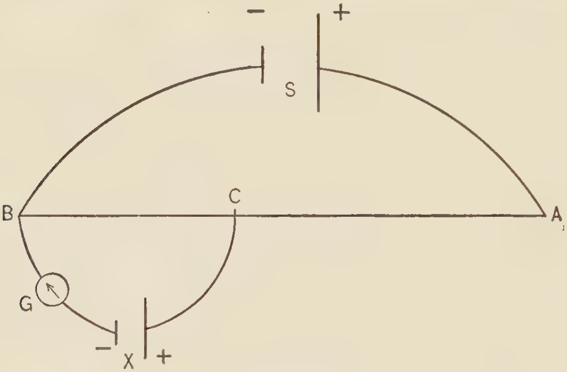

FIG. 19.—Principle of the potentiometer.

| | |
|---|---|
| S, storage battery. | G, galvanometer. |
| AB, slide wire. | X, cell of unknown E.M.F. |
| C, sliding contact. | |

When we consider the circuit CXGB we have two different electromotive forces, namely, $E_{CB}$ between C and B, and that of X, which furnish current in opposite directions. C is now moved along AB until the null-point instrument, G, indicates that no current is flowing through CXGB. Under these conditions the E.M.F. of X is equal to $E_{CB}$.

Since the wire AB is of uniform section, the difference in potential between A and B is equal to:

$$\frac{BC}{AB} \times E,$$

where E is the electromotive force of the battery. $\frac{BC}{AB}$ is the ratio between the resistances of BC and AB. When we are working with a slide wire this ratio is equal to that of the lengths of BC and AB. If the total length of AB is equal to 1000 mm. (or other units of length) as is usually the case, then for $e$, the unknown E.M.F. of X, we have:

$$e = \frac{\mathrm{BC}}{1000}; \quad \mathrm{E} = \frac{a}{1000}\mathrm{E}.$$

$E$ is unknown in this case, but it may be determined easily by switching X out of the circuit and putting in its place a standard cell of known E.M.F. (such as a Weston cell or cadmium normal element. *Cf.* p. 134).

For practical potentiometric titrations it is not necessary to know the value of E, provided it remains constant during the titration, because we only wish to determine the changes in $e$. Hence it is sufficient to determine the values of BC, or $a$, during the titration, or to calculate the ratio, $\frac{\mathrm{BC}}{\mathrm{AB}}$, between the resistances. If, however, it is desired not only to determine the position of the equivalence-point, but also to study the shape of the titration curve from a theoretical point of view, the authors suggest that the real value of $e$ should be included in each new description of a potentiometric titration.

**2. General Equipment for Potentiometric Measurements.**—The storage battery, or accumulator, is a convenient and reliable source of current for the potentiometer. When it has been discharged to an E.M.F. below 1.9 volts it must be recharged. The ordinary direct-current lighting system may be used for recharging if proper resistance be placed in series with the battery (*cf.* text-books on electrochemistry). If a lighting circuit that delivers alternating current is used for this purpose, a rectifier is necessary. There are cheap and convenient types of rectifiers available for charging accumulators. It should be remembered that a freshly charged accumulator changes its E.M.F. a little during the first minutes of its discharge. Therefore, it is recommended that the accumulator be allowed to discharge for a period of about ten minutes before it is used with the potentiometer system. The potentiometer system ACB will be discussed in a special section.

*Standard Cells.*—The Weston cell is usually used as a standard. The construction of this cell is illustrated in Fig. 20. The "normal" Weston cell contains a solution of cadmium sulphate which is saturated at all temperatures at which the cell is used; the cell should therefore contain crystals of the sulphate. The ordinary commercial cell, sometimes called the Weston portable cell, has a cadmium sulphate solution which is saturated at about 4° C. The positive pole of the cell is of pure mercury and is covered with a layer of a paste of mercurous sulphate intimately mixed with mercury. The negative pole is composed of an amalgam containing 12.5 per cent of cadmium by weight. The amalgam is formed by heating mercury over a steam bath and stirring in the cadmium. For the purification of the different materials and the preparation of the Weston cell, see W. M. Clark[1] and Ostwald-Luther.[2]

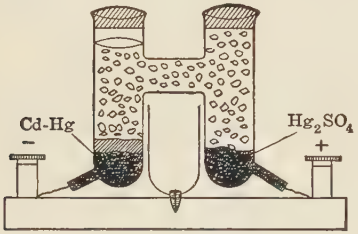

Fig. 20.—Weston standard cell.

The temperature coefficient of the normal Weston cell, which contains an excess of cadmium sulphate crystals, is very small. The E.M.F. is

$$1.01830 + 0.00004(20 - t^\circ),$$

between 15° and 25°.

A thorough study of the unsaturated cadmium cell—its preparation, temperature coefficient, etc., has been made by Vosburgh and Eppley.[3] They find that the cell, when calibrated against the normal Weston cell (saturated), makes a convenient standard of E.M.F. whose value remains constant to 0.02 per cent for years, with proper care. The chief advantage of the cell is that its temperature coefficient is practically negligible, being less than $-0.00001$ volt per degree.

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[1] W. M. Clark, The Determination of Hydrogen Ions, 2d Edition, Williams and Wilkins Co., Baltimore, Md.

[2] Ostwald–Luther, Physiko-Chemische Messungen, 3d Edition, 1910 and 1922, p. 419; R. Luther and K. Drucker, Akad. Verlagsges. m. C. H., Leipzig.

[3] Vosburgh and Eppley, J. Am. Chem. Soc., **45**, 2268 (1923); **46**, 104 (1924); J. Opt. Soc. Am. and Rev. Sci. Insts., **9**, 65 (1924). Vosburgh, J. Am. Chem. Soc., **47**, 1255 (1925); J. Opt. Soc. and Rev. Sci. Insts., **11**, 59 (1925).

*Null-point Instruments.*—The finest and most sensitive null-point instruments are not required for the purposes of potentiometric titrations, because the measurements are comparatively rough. A deflection of one millimeter for one megohm (one million ohms) and an E.M.F. of one volt is generally sufficient. The well-known d'Arsonval galvanometer is not a practical instrument for these measurements.

*a.* The galvanometer is a current-indicating instrument which usually consists of a coil of wire in the magnetic field of a strong permanent magnet. This coil is introduced into the circuit in which the presence or absence of current is to be detected. A current flowing through the turns of the suspended coil produces a magnetic field which, by its interaction with the field of the permanent magnet, tends to turn the coil so that it will embrace the maximum number of lines of force.

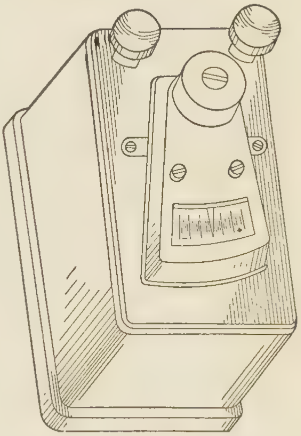

FIG. 21.—Portable Leeds and Northrup Galvanometer.

A small portable galvanometer, such as is furnished by The Leeds and Northrup Company, will serve for most titrations. The sensitivity of this inexpensive galvanometer is such that the current at one volt, acting through a resistance of one megohm, causes the pointer to move one millimeter over the scale. The resistance of the instrument is about 225 ohms. and its period is about 2.5 seconds.

For the titration of very dilute electrolytic solutions, which have a rather high resistance, the sensitivity of this instrument is not high enough. The " portable lamp and scale " galvanometer of The Leeds and Northrup Company will usually serve. This instrument is illustrated in Fig. 22. Its sensitivity is twenty times greater than that of the simple instrument. The "type P" galvanometers of The Leeds and Northrup Company are very easy to set up, are much more sensitive, and are also quite cheap.

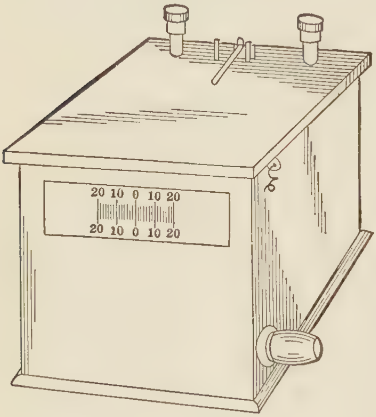

Fig. 22.—Leeds and Northrup lamp and scale galvanometer.

*b.* The capillary electrometer is an instrument that indicates a difference of potential between its poles. It has the advantage of being very inexpensive. The Ostwald-Luther type, which is in common use, is illustrated in its practical form in Fig. 23.[4] Clark gives the following description:

"The capillary electrometer depends for its action upon the alteration of surface tension between mercury and sulphuric acid with alteration of potential difference at the interface. Platinum contacts are sealed into two test-tubes and the tubes are joined together by a capillary, K, of about 1 mm. diameter. After a thorough cleaning, the instrument is filled as illustrated with clean distilled mercury, sufficient mercury being poured into the left tube to bring the meniscus in the capillary near a convenient point. In the other tube is placed pure 10 per cent sulphuric acid. The air is forced out of the capillary with mercury until a sharp contact between mercury and acid is obtained in the capillary." The instrument is now mounted before a microscope, or powerful lens. The latter suffices for most practical purposes. "The definition of the mercury meniscus is brought out by cementing a cover glass to the capillary with Canada balsam." (See Fig. 23.)

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[4] Partly taken from Erich Müller, Die Elektrometrische Massanalyse, p. 4. *Cf.* also W. M. Clark (*loc. cit.*); and Ostwald-Luther (*loc. cit.*).

"An important feature in the use of the capillary electrometer is its short-circuiting between measurements." This is done by the key illustrated in Fig. 23. "Tapping down on the key breaks the short-circuit and brings the terminals of the electrometer into circuit with the E.M.F. to be balanced. If the E.M.F. is out of balance, the potential difference at the mercury-acid interface causes the mercury to fall or rise in the capillary. Releasing the key short-circuits the terminals and allows the mercury to return to its normal position. Adjustment of the potentiometer system is continued till no movement of the mercury can be detected."

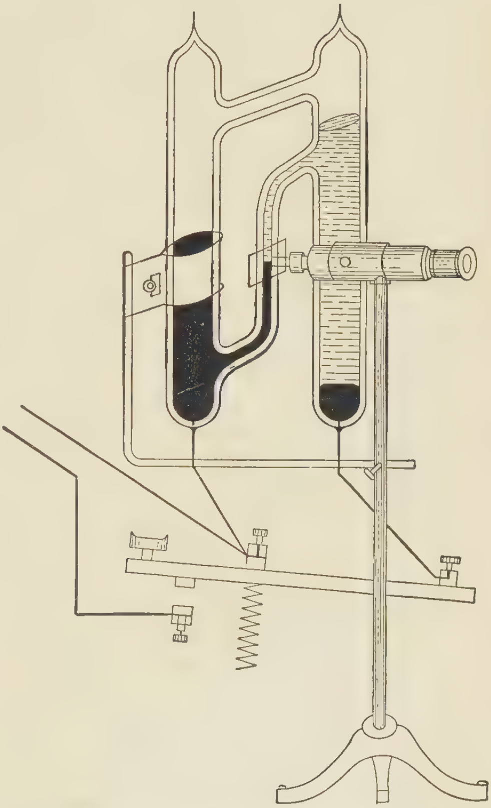

FIG. 23.—Capillary electrometer with microscope.

When the capillary electrometer has been switched into the circuit for too long a time, polarization may occur, with the formation of fine gas bubbles in the capillary. In this case a fresh contact must be secured between the mercury and the acid in the capillary, by inverting the apparatus. As a result of this manipulation, the mercury streams through the capillary, breaks suddenly, falls, and forms a fresh surface. A fresh surface must also be made in cases where the surface between mercury and acid has become dirty, as this condition makes it impossible to see a sharp change in the meniscus when there is only a small potential difference. Sometimes it is advantageous to use a small 2-volt lamp behind the electrometer for clearer observation of the surface in the capillary.

*The Cell of which the E.M.F. is to be Determined.*—This is built up of the unknown indicator electrode and a standard half-cell. The shape and material of the indicator electrode depends upon the kind of ion of which the concentration is to be determined. A more detailed survey of *standard half-cells* is given in the section entitled " Special Determinations." (*Cf.* p. 164.)

*Calomel Electrodes.*—These are generally used as standard half-cells.[5] A calomel electrode is one in which mercury and calomel are overlaid with a potassium chloride solution of definite concentration. The mercury and calomel must be as pure as possible (*cf.* the corresponding chapters in W. M. Clark, *loc. cit.*). A layer of the pure mercury is placed on the bottom of the electrode vessel, and upon this is put a layer of mercury and calomel paste in the potassium chloride solution. This mixture may be obtained by rubbing the mercury and calomel together in a mortar so that the mercury is in a very finely divided state, and the mixture has a black or grayish-black appearance. The mixture is washed several times with the potassium chloride solution with which the vessel is to be filled. After the last decantation the mixture is placed upon the mercury layer in the vessel.

The best method for the preparation of the mixture of calomel and mercury is the electrolytic one devised by Lipscomb and Hulett [6] and recently simplified by W. W. Ewing.[7]

The potassium chloride solution, with which the electrode is filled, must be saturated with calomel. Therefore, it is recommended that this solution be shaken with the mercury-mercurous chloride paste for some time. W. M. Clark, in his excellent book, gives descriptions and illustrations of the different calomel electrode vessels that have been described in the literature. This standard work may be consulted for further details. For practical work in potentiometric titrations, the authors prefer the simple form that is used by Erich Müller.[8] Kolthoff has used this vessel for several years, and considers it the most convenient one for potentiometric titrations.

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[5] Stig Veibel, J. Chem. Soc., **123**, 2203 (1923), recommends the use of the quinhydrone electrode in 0.01 N hydrochloric acid and 0.09 N potassium chloride as a reference electrode.

[6] G. T. Lipscomb and G. A. Hulett, J. Am. Chem. Soc., **38**, 22 (1916).

[7] W. W. Ewing, J. Am. Chem. Soc., **47**, 301 (1925).

CE, the calomel electrode, is a wide-mouthed bottle. A layer of mercury about 0.5 cm. deep is put on the bottom; above this is placed the mercury-calomel paste, and the bottle is filled with the potassium chloride solution, saturated with calomel. (The authors always use 1 N KCl.) The bottle is closed by a two-holed rubber stopper. Through one of the holes passes a capillary tube partly filled with mercury; a platinum wire is sealed in at the bottom of the tube. A copper wire, which makes contact with the circuit, dips into the mercury in the capillary. The capillary is so placed that the platinum wire dips into the mercury of the electrode.

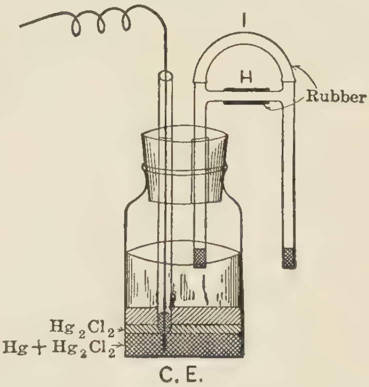

FIG. 24.—Calomel electrode and salt bridge; type recommended by E. Müller.

Through the other hole of the stopper passes the siphon, which makes electrolytic contact with the solution to be titrated. The latter is placed in a beaker. The siphon is made of two glass T-tubes which are joined by a rubber tube at H, and also by a longer rubber tube at I. The two tubes are closed at the bottom by plugs of filter paper and are then filled up with saturated potassium chloride solution, so that there is contact between the left and right legs. The plugs are made of high-grade filter paper, which is moistened with the potassium chloride solution, rolled between the fingers, and pressed into the tubes. In this way there is practically no leakage or diffusion of solution from the tubes to the liquids in the electrode bottle or beaker, respectively. If the filter paper is well pressed in, the siphon may be kept for several weeks before it needs to be refilled.

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[8] *Loc. cit.*, Die Elektrometrische Massanalyse.

Dr. H. Meusel of Dresden (private communication) fills the ends of the siphon tube, which joins the beaker and calomel electrode, with a warm solution of 3 g. agar in N potassium chloride. This solution forms a stiff gel, upon cooling. The rest of the siphon is filled with an aqueous solution of potassium chloride. The agar-KCl gel has a high conductivity. It therefore eliminates the slow establishment of steady potential that occurs when the ends of the siphon are filled with filter paper.

Another calomel electrode, of convenient shape, which may be placed directly in contact with the solution to be titrated, without the use of a salt bridge, has been described recently by C. J. Schollenberg.[9]

In titration with, or of, silver and mercury salts, it is recommended that the siphon be filled with potassium nitrate or sulphate, or with ammonium nitrate, rather than with potassium chloride solution. When the calomel electrode is not in use, the hole through which the siphon passes is closed by a small rubber stopper in order to prevent evaporation of the solution in the vessel.

As far as practical titrations are concerned, we may leave the liquid-junction potentials out of consideration. In practice, four different calomel electrodes are used, i.e., they are filled respectively with potassium chloride solutions of four different concentrations. On the reproducibility of these electrodes the reader is referred to W. M. Clark, *loc. cit.*, where a full discussion of the literature is given. Since all of our standard values are referred to the normal hydrogen electrode, it is of importance to know the potential difference between the different calomel electrodes and the normal hydrogen electrode. The following values are taken from the data given in Clark's book and in the excellent paper of S. P. L. Sörensen and K. Linderström-Lang:[10]

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[9] C. J. Schollenberg, J. Ind. Eng. Chem., **17**, 649 (1925).

0.1 N calomel electrode—N hydrogen electrode: $-0.3380+0.00006(t-18)$
1.0 N calomel electrode—N hydrogen electrode: $-0.2864+0.00024(t-18)$
3.5 N calomel electrode—N hydrogen electrode: $-0.2549+0.00039(t-18)$
Saturated calomel electrode—N hydrogen electrode: $-0.2504+0.00065(t-18)$

0.1 N means that the electrode is filled with 0.1 N potassium chloride solution, etc.

From this table one might get the impression that the temperature coefficient of the 0.1 N calomel electrode was the smallest, and that the temperature coefficient increased with increasing potassium chloride concentration. This is not true, because we are not considering the calomel electrode alone, but rather cells which include the normal hydrogen electrode. Hence, the temperature coefficient of the cell is the algebraic sum of those of the two electrodes. From the measurements of Sörensen *et al.* (*loc. cit.*) we know that the temperature coefficient of the hydrogen electrode is −0.00085. Introducing this value, we obtain the following temperature coefficients:

0.1 N calomel electrode, 0.00079
1.0 N calomel electrode, 0.00061 (Richards, 1897)
3.5 N calomel electrode, 0.00046
Saturated calomel electrode, 0.00020

The authors generally use the normal calomel electrode as a reference electrode, and they always refer the values of the electromotive force for the titration curves to this electrode unless they make a special note to the contrary. By means of the above data these values may be readily recalculated to the basis of the normal hydrogen electrode.

**3. The Potentiometer System.**—(*a*) In the discussion of the principle of the potentiometric method (*cf.* Fig. 19, p. 132) AB represents a slide wire such as is used in conductivity work. Such a slide wire, with its rather low resistance, can not be recommended for very accurate measurements. It is more than sufficient for our titration work, since we wish to know the change of the potential during the titration, and a small error in the absolute of the E.M.F. is without influence on the result. Therefore, one of the authors (Kolthoff) generally uses a slide wire—not the ordinary one, but the so-called *Walzenbrücke* (cylinder bridge) of Kohlrausch. This instrument is very convenient and occupies little space. In this case the wire is of considerable length and is wound on a drum of hard rubber or other insulating material. Sliding contact is effected by means of a small roller which travels along the wire. When the system is balanced, the E.M.F., $e$, of the unknown element is:

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[10] S. P. Sörensen and K. Linderström-Lang, Compt. rend. du Lab. Carlsberg **15**, (1924). On the saturated electrode, *cf.* W. W. Ewing, J. Am. Chem. Soc., **47**, 301 (1925). For literature references see I. M. Kolthoff, Chem. Weekblad (1925).

$$e = \frac{a}{1000}\text{E},$$

where $a$ is the value read on the wire and E is the E.M.F. of the battery. By placing a resistance between one of the ends of the bridge and the battery and switching in the standard cell, it is easy to adjust E at 2 volts; under these conditions we have:

$$e = a \times 2 \text{ millivolts.}^{11}$$

(*b*) Instead of the slide wire, Erich Müller[12] prefers the use of the Ostwald "decade" rheostat. This apparatus has been described by Ostwald and Luther.[13] The instrument is illustrated in Fig. 25.

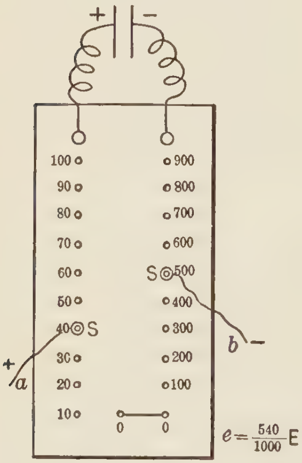

FIG. 25.—Ostwald decade rheostat.

It is of practical convenience to have a total resistance of 1000 ohms. By means of two plugs, S, resistance may be switched into

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[11] *Cf.* also Roberts, J. Am. Chem. Soc., **41**, 1358 (1919).

[12] Erich Müller, Die Elektrometrische Massanalyse, 2d Ed., p. 3.

[13] Ostwald-Luther, Physiko-Chemische Messungen, p. 427.

the side circuit until the system is balanced. If this resistance is equal to $a$, we again have:

$$e = \frac{a}{1000}E.$$

*c.* For work of a high order of accuracy, two precision resistance boxes, each with a total resistance of about 10,000 ohms, should be used. In order to keep the current constant, any resistance removed from one of the boxes is added to the other, and conversely. In this case the total resistance is always constant.

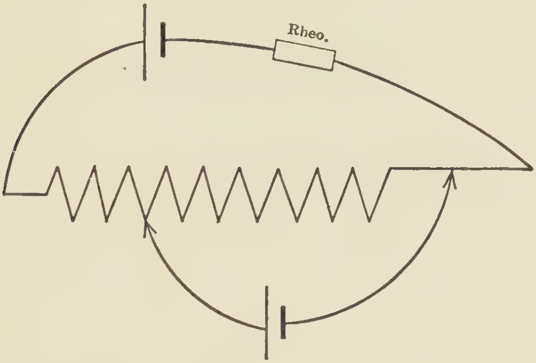

FIG. 26.—Principle of the potentiometer.

*d.* The use of the so-called "potentiometers" is of great practical advantage. From a didactic standpoint they have the disadvantage of giving E.M.F. readings without forcing the student to understand what he is doing. On the other hand, the convenience of these instruments is so great that they will gradually find a place in all laboratories for electrometric work. A description of the "student's potentiometer" of The Leeds and Northrup Company[14] is given below. This instrument is of sufficient accuracy for all titration work. The authors can not recommend the same company's much more accurate type-K potentiometer for work of this kind, as it is too sensitive. The principle of the instrument was discussed in § 1; it is represented diagrammatically in Fig. 26. *Rheo.* is a resistance box.

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[14] The Leeds and Northrup Company, Bulletin No. 765.

Figure 27 gives the complete wiring diagram of the student's potentiometer. The essential part of the instrument consists of twenty-two 100-ohm coils, in series with which is an extended slide wire having a resistance of 100 ohms. One contact point is so arranged that it can make contact between any two of the 100-ohm coils, and a second point can be brought into contact with any point on the wire. The terminals of the total resistance of 2300 ohms are brought out to a pair of binding posts. The scale of the extended wire is divided into 1000 equal parts. A second pair of binding posts leads to the two sliding contacts.

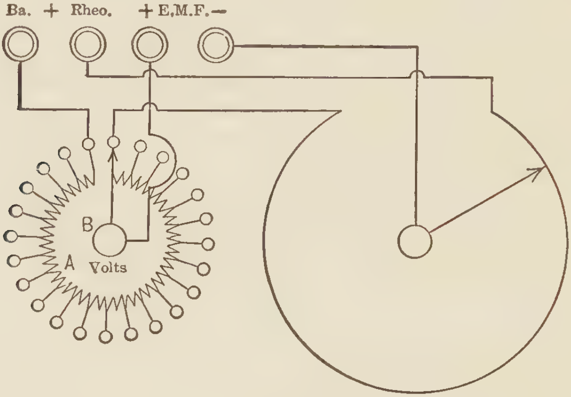

Fig. 27.—Leeds and Northrup students' potentiometer.

The resistance box (Fig. 28) is an auxiliary apparatus which has a resistance of at least 1000 ohms, variable in steps of 1 ohm.[15] Two dry cells in series are used as the source of current.

To make a reading, set the potentiometer switches to correspond to the voltage of the standard cell. Connect the standard cell in the circuit by means of the double-throw switch, and adjust the regulating resistance until the galvanometer is balanced. By this process the E.M.F. supplied by the dry cells is adjusted to 2.300 volts. Now, since the total resistance between the terminals O B is 2300 ohms, each ohm corresponds to an E.M.F. of 0.1 millivolt. To make a reading of an unknown cell, proceed as follows: reverse the double-throw switch so that the potential to be measured is brought into the circuit. Now manipulate the two dials of the potentiometer until no current flows through the galvanometer. The " unknown " E.M.F. may then be read off directly. For example, if the dial switch is on 0.6 and the slide wire on .0612, the reading is .6612 volt. The calibration of the slide wire is guaranteed to be accurate to 0.5 per cent; the measurements may be in error by 0.0005 volt. Figure 28 gives the wiring diagram of the student's potentiometer as connected for measurement of a potential difference. The advantages of the instrument are that a balance is very quickly obtained and the unkown E.M.F. may be read without making any calibration. The authors have found this set-up very convenient for ordinary analytical work as well as for the investigation of new problems.

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[15] Special regulating resistances may be obtained which are less expensive than the 3-dial resistance box.

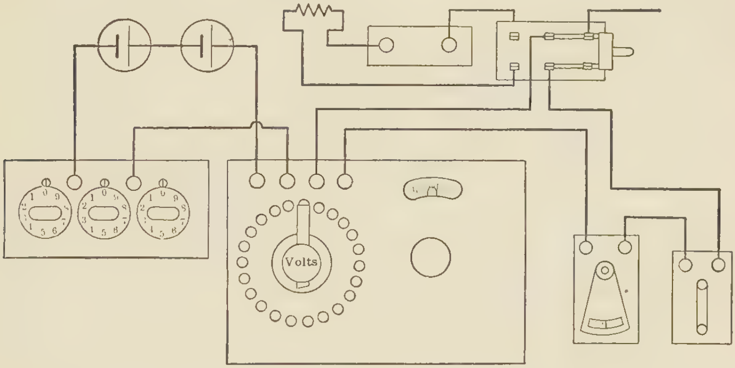

FIG. 28.—Leeds and Northrup students' potentiometer and accessories.

(*e*) Another mode of using a simple system without calculation depends on the use of the millivoltmeter.[16] This may be done in various ways. Consider Fig 19, p. 132. We may use for resistance, AC, a decade resistance box of high resistance (50,000 ohms). This resistance box need not be accurate. The millivoltmeter is placed between C and B. This instrument usually has a resistance of about 1000 ohms. The resistance in AC is changed until the system is balanced, and the E.M.F. is read directly on the voltmeter. Another arrangement is shown in Fig. 29.

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[16] *Cf.* J. H. Hildebrand, J. Am. Chem. Soc., **35**, 847 (1913).

Kling and Lassieur [17] recommend a similar arrangement in which they use two sliding resistances, one of 195 ohms, the other of 5 ohms for the finer adjustment. After the system is balanced, the resistances are switched out and the voltmeter is switched in.

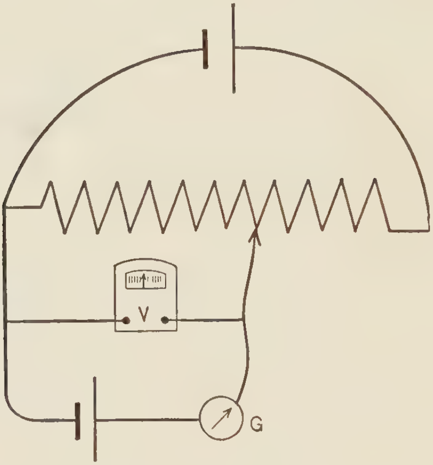

Fig. 29.—Potentiometer arrangement suggested by Hildebrand.

The apparent advantage of the use of the millivoltmeter lies in the fact that the standard cell may be omitted, as it is not necessary to know the E.M.F. of the source of current; moreover, the resistance values need not be known. The disadvantages are that millivoltmeters are usually provided with a scale of 10 millivolts per division, hence the millivolt readings must be approximated; moreover, recalibration of the instruments is necessary.

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[17] Kling and Lassieur, Compt. rend., **174**, 165 (1922).

# CHAPTER VIII

## DETECTION OF THE END-POINT OF A POTENTIOMETRIC TITRATION

**1. General and Exact Method.**—Since the abrupt change in potential occurs very close to the equivalence-point, the latter may be easily found by plotting the change of the E.M.F. against volume of reagent. It is usually assumed that the inflection-point, i.e., the middle of the jump in potential, indicates the equivalence-point precisely. We have seen in Chapters V and VI that, especially in oxidation-reduction reactions where we are titrating with substances such as permanganate, bichromate, etc., the equivalence-point is not located at the middle of the break, but very near the end where the curve bends toward the permanganate or bichromate side. The potential break, however, is usually very steep, and therefore the method above described is satisfactory for most practical cases when we are titrating with sufficiently concentrated solutions. It enables us to locate the point of inflection by inspection with the desired degree of accuracy.

It is not necessary, however, to plot all the data of the titration curve, since only the change near the end-point is of analytical importance. The method which was proposed by Hostetter and Roberts [1] is more accurate as well as simpler; it is to make a graph of the values of $\frac{\Delta E}{\Delta c}$ against cubic centimeters of reagent. The maximum of this curve indicates the equivalence-point. It is not necessary to make a graph, as the maximum may be read directly from a table. This is done in the following way: In the vicinity of the equivalence-point we add the reagent drop by drop and determine the potential each time. We may then calculate the value of $\frac{\Delta E}{\Delta c}$ after the addition of each drop of reagent; the maximum is found with an accuracy of at least half a drop of reagent. The drop volume must, of course, be known. When, for example, we find the following values for $\frac{\Delta E}{\Delta c}$:

---

[1] Hostetter and Roberts, J. Am. Chem. Soc., **41**, 1337 (1919).

| | $\frac{\Delta E}{\Delta c}$ |
|---|---|
| 1 drop | 200 |
| 1 drop | 400 |
| 1 drop | 900 |
| 1 drop | 800 |
| 1 drop | 600 |

the maximum is located between the third and fourth drops and we may approximate it at $3\frac{1}{2}$ drops with an accuracy of 0.01 cc. of reagent. The following example gives the results of an actual determination:

TITRATION OF 25 CC. OF POTASSIUM IODIDE (ABOUT 0.1 N), MIXED WITH 150 CC. WATER AND 5 CC. 4 N SULPHURIC ACID, WITH PERMANGANATE

(E.M.F. Measured Against N Calomel Electrode)

| Cubic Centimeters of Permanganate | E | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|
| 24.0 | 0.482 | |
| 24.28 | 0.504 | |
| 24.36 | 0.518 | |
| 24.39 | 0.528 | 330 |
| 24.42 | 0.544 | 530 |
| 24.46 | 0.588 | 1000 |
| 24.49 | 0.740 | *5070 Maximum* |
| 24.52 | 0.752 | 400 |
| 25.00 | 0.772 | 40 |

Maximum $\frac{\Delta E}{\Delta c}$ : *24.48* cc. reagent.

**2. The Pinkhof Method and Its Modifications.**—J. Pinkhof,[2] who made an excellent study of the application of potentiometric titrations, attempted to devise a simple arrangement whereby the method could be generally applied without being at all expensive. He replaced the calomel electrode by a compensation electrode whose potential is exactly equal to that of the unattackable electrode solution at the completion of the titration. When this method is employed, a sudden reversal of polarity marks the end-point. Hence, no potentiometer system is necessary and a simple capillary electrometer serves as indicating instrument. The arrangement is illustrated in Fig. 30.

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[2] J. Pinkhof, Over de Toepassing der Elektrometrische Titraties, Dissertation, Amsterdam (1919).

The mercury of the capillary electrometer moves in one direction, when the instrument is switched into the circuit, until the equivalence-point is reached; at this point it ceases to move. With an excess of the reagent, the mercury moves in the opposite direction. A preliminary titration is usually necessary because we have no indication as to whether we are close to the end-point.

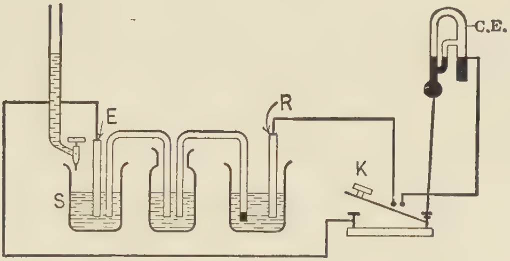

FIG. 30.—The Pinkhof system.

S, solution to be tested.
E, indicator electrode.
R, reference electrode.
K, tapping key.
C.E., capillary electrometer.

The arrangement has a number of disadvantages: every titration requires its own peculiar electrode system; and it is difficult to compensate for the effects of foreign electrolytes in the solution, and for temperature influence. As above mentioned, there is no warning of the approach of the end-point.

W. D. Treadwell[3] uses a half-cell which contains a solution of the same composition as that which the solution to be titrated will possess at the equivalence-point; this solution is in contact with the same unattackable electrode, instead of the standard electrode. Treadwell uses a millivoltmeter instead of a capillary electrometer. The arrangement is illustrated in Fig. 31. The reader is referred to the original paper for details.

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[3] W. D. Treadwell and L. Weiss, Helv. Chim. Acta, **2**, 680 (1919); see also Garner and Waters, J. Soc. Chem. Ind., **41**, 337 (1922); Oesterheld and Honegger, Helv. Chim. Acta, **2**, 398 (1919).

The disadvantage again lies in the necessity of preparing a different end-point electrode for each reaction. This objection can not be brought against the modification which Erich Müller [4] has devised. He uses the normal calomel electrode as a reference electrode; at the beginning of the titration he switches into the circuit an electromotive force which is just equal to that developed by the indicator system at the end-point. The reagent is added until the null-point instrument shows no deflection, or reverses the direction of the deflection. It is more practical and convenient to use a rough and inaccurate potentiometer system and to switch in the voltmeter from time to time. (Principle of

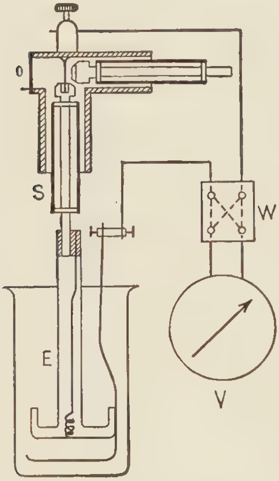

Fig. 31.—Treadwell system

W, commutator.
V, voltmeter.
E, electrode.
S, stirrer.

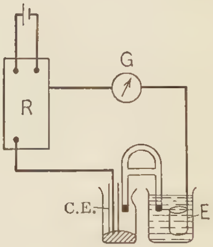

Fig. 32.—Müller system.

E, indicator electrode.
C.E., normal calomel electrode.
G, galvanometer.
R, Ostwald decade rheostat.

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[4] Erich Müller, Die Elektrometrische Massanalyse, 2d Ed., p. 78.

Kling and Lassieur, *loc. cit.*, *cf.* p. 146). Reagent is added until the voltmeter indicates the equivalence-potential.

Hence we need to know the value of the equivalance-potential, which must be determined by the method above described (§ 1). The Müller arrangement is more expensive than that of Pinkhof. We again have the disadvantage that the influence of foregin salts upon the equivalence-potential must be taken into account. When the jump in potential at the equivalence-point is very large, this influence may be ignored; however, when we are dealing with the successive titration of various substances in a solution, the concentration of foreign electrolytes may be of very great importance. In oxidation-reduction titrations with substances like permanganate, bichromate, etc., the hydrogen-ion concentration of the liquid to be titrated is of especially great importance. Another disadvantage of the Müller arrangement is that there is no warning of the approach of the end-point.

The Pinkhof method, and its modifications, all have this advantage in common: that the titration may be performed very quickly. A result may be obtained in about two minutes. This rapidity, however, carries with it a marked disadvantage, namely, that we have no assurance that the potential has become constant, and that equilibrium has been established. Everyone who has had experience with the performance of potentiometric titrations knows that, near the equivalence-point especially, where the break in potential occurs, the potential does not become constant immediately after the addition of the reagent. It is necessary to wait a longer or shorter period for the establishment of equilibrium. Hence, when we add reagent until the equivalence-potential is reached we have no assurance that the equivalence-point is reached, and an erratic result may therefore be obtained. Another disadvantage of the Pinkhof system is that it is balanced at the equivalence-point only; therefore, polarization may occur at a distance from this point.

*For all the above-mentioned reasons, the authors can not recommend the Pinkhof system and its modifications for accurate titrations.* In some particular instances it may be of distinct advantage; in general, however, the method described in § 1 is recommended.

When the potential becomes constant very soon after the addition of reagent, the titration may be carried out in about five minutes. If the establishment of equilibrium is slow, much time is required for a titration, but the method has the advantage of giving accurate results. The time may always be shortened by adding the reagent in a stream until the potential begins to change rapidly. This gives an indication that we are approaching the equivalence-point, and further addition of the reagent must proceed slowly as described in § 1. This simplification must be applied carefully, since it is possible to overstep the end-point in this way in cases where the jump in potential is small. Those who have had some experience with potentiometric titrations will readily find, in any particular instance, the conditions under which an accurate result is most quickly obtained. The authors wish to lay stress on the accuracy which may be attained by the application of potentiometric titrations. The literature contains reports of many investigations in which *rapid potentiometric determinations are described.* Unfortunately, this practical advantage is often gained at the cost of accuracy. The reader is warned against applying these methods unless it has been proved by the exact method that the results are reliable.

In all cases where a new titration method is being investigated, the whole titration curve should be determined, since many theoretical and practical conclusions may be drawn from its form.

**3. The Dutoit System. Polarized Indicator Electrode.**—As we have seen on page 125, it is inconvenient or impracticable to use an electrode of the corresponding metal in many precipitation reactions. In such instances Dutoit and von Weisse[5] have proposed the use of a cathodically polarized platinum electrode in conjunction with the usual calomel half-cell. A fresh laywer of metal is formed continuously, by the feeble polarizing current, on the platinum cathode, which then gives the characteristic electrode potential of the metal. The apparatus is indicated in Fig. 33.

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[5] Dutoit and von Weisse, J. chim. phys., **9**, 578 (1911).

The experimental set-up is not simple. There is a loss of metal due to the polarization, and hence the result is not accurate. In spite of these disadvantages, the arrangement sometimes makes possible the estimation of a number of cations in a given solution by the addition of appropriate reagents in succession. The method can not be recommended, however, for general application, nor for particularly accurate determinations.

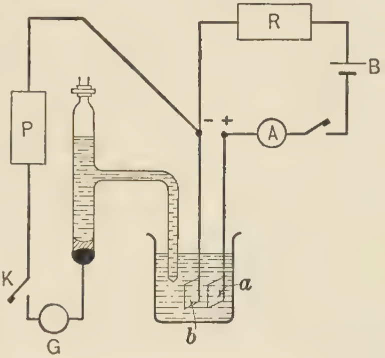

FIG. 33.—Polarization system of Dutoit and von Weisse.

*a*, auxiliary platinum electrode.
*b*, cathodically polarized platinum electrode.
B, polarizing battery.
A, ammeter for polarizing current.
R, resistance.
P, potentiometer.
G, galvanometer.

**4. Polarized Bimetallic Electrode Systems.**—*Bimetallic Systems.*—In connection with a potentiometric study of the ferrous iron—bichromate reaction, Hostetter and Roberts[6] made the important observation that a cell consisting of a palladium electrode and the usual calomel half-cell did not exhibit any appreciable change in potential at the equivalence-point. They therefore suggested that a cell composed of one platinum and one palladium electrode might serve for the determination of end-points, the platinum wire being the indicator electrode.

Willard and Fenwick[7] made an extensive investigation of the characteristics of bimetallic systems. Their general findings may be summarized as follows:

The initial difference in potential between two dissimilar metal electrodes, in the absence of an oxidizing agent, varies considerably with the nature of the pre-treatment of the electrodes, and with the concentration of acids, salts, etc., in the solution. Upon addition of oxidizing agent, the potential difference falls rapidly to practically zero and remains thus until within 0.2–0.3 cc. of the end-point. A short rise in the potential difference gives warning of the abrupt and characteristic break in potential at the end-point. This break usually amounts to 100–200 millivolts. The most effective systems were found to consist of platinum, together with some other metal or alloy of metals of the platinum group, or with tungsten. Palladium and palladium alloys were found to be unsatisfactory because of the solubility of palladium in various solutions.

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[6] Hostetter and Roberts, J. Am. Chem. Soc., **41**, 1337 (1919).

[7] Willard and Fenwick, J. Am. Chem. Soc., **44**, 2504 (1922). See also Florence Fenwick, The Theory and Application of Bimetallic Electrode Systems in Electrometric Analysis, Dissertation, University of Michigan (1922).

A further study of the behavior of systems of two dissimilar metallic electrodes during the course of titrations has been made by Van Name and Fenwick.[8] They point out that since the ideal expression for the electrode potential, E, of an inert electrode is of the form:

$$\mathrm{E} = \text{Const.} \cdot \frac{x}{1 - x},$$

where $x$ is the fraction in the higher, and $1-x$ that in the lower state of oxidation, the value of E is extremely sensitive to slight changes in $x$ when it approaches the limiting values 0 and 1 at the beginning of a titration and at the equivalence-point respectively.

If there is a difference between the relative rates at which the two dissimilar electrodes tend to approach equilibrium, the divergence will be greatest in these two regions of maximum sensitivity. Experiment shows that this is the case. The divergence is more frequently observed at the equivalence-point, presumably because it is very difficult to prepare an oxidant that is entirely free from its reduction product, and conversely.

The end-point potential divergence is really a time effect which is caused by the difference in the rates at which the dissimilar electrodes approach equilibrium. Given sufficient time, both electrodes would presumably reach the same state of equilibrium and the potential difference would vanish. The general tendency is in this direction, but the difference may persist for a long period.

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[8] Van Name and Fenwick, J. Am. Chem. Soc., **47**, 9 (1925).

*Differential Titration with Platinum Electrodes.*—D. C. Cox [9] has described a method of differential titration which gives an end-point indication analogous to those obtained with bimetallic electrode systems. The method consists in titrating two similar portions of a given solution, with an appropriate reagent, at slightly different rates: one burette may have delivered 0.1 or 0.2 cc. more of reagent to the first solution than the second burette has delivered to its solution. The difference in rate is called the " offset." An offset of 0.2 cc. is generally convenient. Similar electrodes, which may be platinum or air electrodes,[10] are placed in the two beakers. Electrolytic connection between the beakers is established by a salt bridge. At the end-point a sharp difference in potential is developed between the two electrodes; the difference is registered by a millivoltmeter, or by a simple potentiometer system. The end-point is at the maximum potential difference. No data are given to establish the limit of accuracy of the method. Cox states that it is simpler and more accurate than the usual methods of electro-titration. He claims the following advantages:

1. No necessity of plotting curves. 2. Elimination of calomel half-cell. 3. Compensation of error due to electrode drift. 4. Elimination of diffusion troubles by using solutions of almost identical compositions.

Cox applied the method to neutralization reactions only. It should be equally applicable to oxidation-reduction reactions, and perhaps to some precipitation reactions.

*Polarized Bimetallic Systems.*—In studying the effect of various modes of pre-treatment upon the behavior of the various metallic electrodes, Willard and Fenwick [11] found that polarization was a very effective method for obtaining a satisfactory

[9] D. C. Cox, J. Am. Chem. Soc., **47**, 2138 (1925).

[10] *Cf.* Furman, J. Am. Chem. Soc., **44**, 2685 (1922); *cf.* p. 212.

[11] Willard and Fenwick, J. Am. Chem. Soc., **44**, 2516 (1922).

behavior. This effect was predicted on the basis of the Nernst-Fredenhagen[12] theory that an unattackable electrode behaves as a gas electrode. Hence, the electrolytic charging of an electrode with either oxygen or hydrogen should cause it to exhibit a steadier behavior than would a random charging caused by immersing the electrode in an oxidizing or reducing solution, heating in a flame, etc. Finally, Willard and Fenwick found that a *polarized bimetallic system, composed of two portions cut from a very pure platinum wire, gave the best end-point indications of any bimetallic system.* The two similar electrodes were polarized anodically and cathodically, respectively, with a very small current (about 0.5 × $10^{-5}$ ampere). The apparatus is shown diagrammatically in Fig. 34.

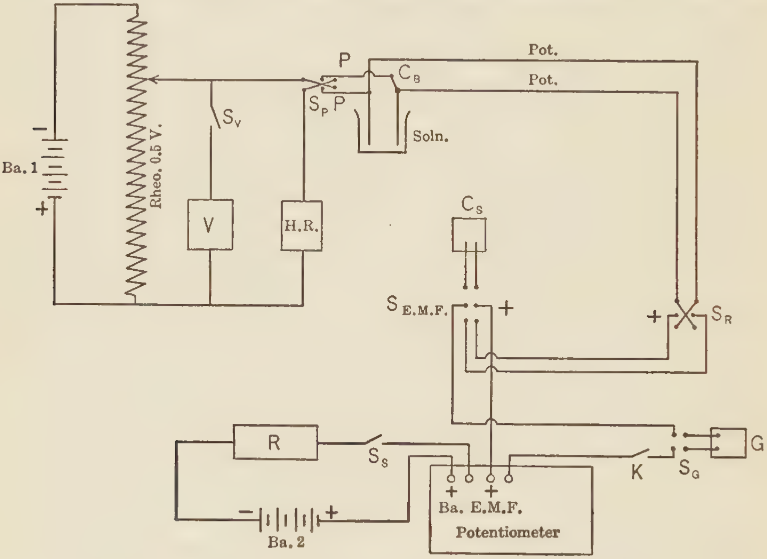

Fig. 34.—Polarized bimetallic system of Willard and Fenwick.

| | |
|---|---|
| $Ba_1$, | storage battery for polarizing current. |
| $Ba_2$, | Edison storage battery. |
| Rheo., | rheostat for taking off polarizing voltage. |
| V, | voltmeter. |
| H.R., | high resistance (100,000 ohms). |
| $S_V$, | voltmeter switch |
| $S_R$ and $S_P$. | reversing switches. |
| P.P., | polarizing leads to electrodes. |
| $C_B$ | mercury cup commutator. |
| Pot.Pot., | leads from electrodes to potentiometer system. |
| $C_S$, | standard cell. |
| $S_B$, | battery switch. |
| $S_G$, | galvanometer switch. |
| G. | galvanometer. |

---

[12] Fredenhagen, Z. anorg. Chem., **29**, 398 (1902); Nernst (1889).

The end-point change is an abrupt break of 100 to 200 millivolts.

The mechanism of the end-point change has been studied further by Van Name and Fenwick.[13] Their conclusions are as follows:

" 1. The principal factor determining the sharpness of the electrometric end-point with polarized electrodes of pure platinum is the difference in the degree of reversibility of the electrode reaction before and after the end-point. Other factors, such as concentration and rate of stirring, are of minor importance. The end-point phenomena are more distinct the more nearly the electrode reactions conform to the requirement of complete reversibility on one side of the end-point and complete irreversibility on the other, but are sharp enough for practical use in analysis in some cases which fall far short of meeting this requirement.

" 2. Although polarization sometimes produces a slight displacement of the end-point break of a single electrode, the errors so introduced are too small to be of significance in volumetric analysis.

" 3. The end-point break in titrations of the ordinary type, based on the single potential of the platinum electrode, may often be improved and the behavior of the electrode made much more dependable and satisfactory by polarizing it with respect to an auxiliary electrode."

The arrangement devised by Willard and Fenwick has the disadvantages of complexity, rather expensive nature of the apparatus, and lack of warning of approach of the end-point. On the other hand, the simplicity of the electrodes themselves and the sharpness of the end-point indication are decidedly favorable. A discussion of the results, which Willard and Fenwick obtained, is given in the section entitled " Special Determinations."

**5. Continuous-reading Potentiometric Devices.**—Instead of reading and plotting the changes in potential, it is possible to have these changes recorded automatically by an instrument of the type that has been perfected for automatic thermocouple records. Such recording instruments may be provided with devices for adding reagent at a given potential reading, or releasing alarm signals, etc. Some of these applications have been described by Keeler.[14] These automatic devices depend upon the successive mechanical balancing of a modified Wheatstone bridge after small changes in potential.

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[13] Van Name and Fenwick, J. Am. Chem. Soc., **47**, 19 (1925).

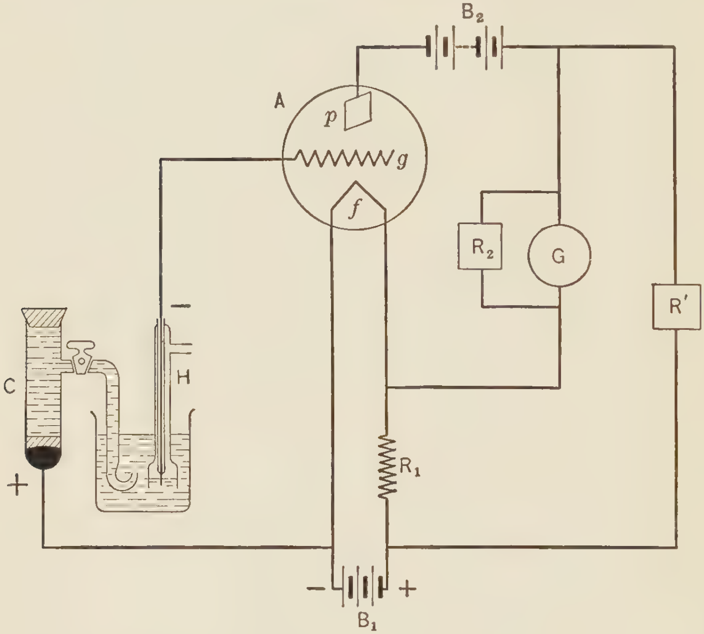

FIG. 35.—Continuous-reading electro-titration apparatus of Goode.

| | | | |
|---|---|---|---|
| H, | hydrogen electrode. | G, | galvanometer. |
| C, | calomel cell. | A, | electron tube. |
| $B_1$, | 6-volt battery. | *p*, | plate. |
| $B_2$, | 22.5 volt battery. | *f*, | filament. |
| $R_1$, | 0.6-ohm resistance. | *g*, | grid. |
| $R_2$, | 25-ohm resistance. | R′, | balancing resistance (about 1300 ohms). |

A new type of continuous-reading potentiometric titration apparatus has been based on the use of the electron tube.

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[14] Keeler, J. Ind. Eng. Chem., **14**, 395 (1922); Power, **55**, 768 (1922). *Cf.* also Rideal, Chemical Age (London), **5**, 232 (1921). *Cf.* Furman, Chap. XIII, p. 860, Taylor's " Physical Chemistry," D. Van Nostrand Co.

Goode[15] was the first to devise such an arrangement for titration purposes. His improved set-up is represented in Fig. 35.

In effect, the apparatus acts as a simple voltmeter which draws almost no current from the titration cell. After the residual plate current has been balanced out by adjustment of R′, if the conditions have been properly chosen, the current of the galvanometer circuit is a linear function (within 1 per cent) of the potential difference which is developed between the electrodes of the titration cell.

Calhane and Cushing[16] were the first to apply an arrangement similar to that of Goode to a precipitation reaction, viz., the determination of chloride in very dilute solution with silver nitrate. Treadwell[17] has also applied a slightly modified apparatus of the same general nature to the precipitation of chloride with silver solution. He uses the electrode system which he devised (*cf.* § 2, and Fig. 31, p. 150). His arrangement differs from that of Goode in the following particulars: The galvanometer is replaced by a voltmeter; a Philips tube Type DI is used instead of the " radiotron " type UV 201 of Goode's apparatus; a potential of 1.6 volts is introduced into the circuit in series between the negative (indicator) electrode of the titration cell, and the grid of the electron tube.

Thus far, there has been no extensive application of the electron tube to potentiometric titrations. The direct-reading feature is made possible by the fact that the tube is essentially a potentiometer which draws virtually no current from the titration cell, nor under proper conditions can any current be supplied to the cell. In the words of Treadwell (*loc. cit.*): " As long as the grid is negative toward the source of the electrons (filament) it is unable to take up electrons. The grid takes up only as much electricity as its small electrostatic capacity will permit at the applied potential. . . . The grid only influences the anode current (plate current) by its electrostatic action."

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[15] Goode, J. Am. Chem. Soc., **44**, 26 (1922).

[16] Calhane and Cushing, J. Ind. Eng. Chem., **15**, 1118 (1923).

[17] Treadwell, Helv. Chim. Acta, 8, 89 (1925).

By making very minor changes, Treadwell also applies his electron-tube arrangement to conductometric titrations.

Goode has described an improved hydrogen-ion meter.[18] This device is in effect a continuous-reading potentiometer. It differs from the apparatus which is shown diagrammatically in Fig. 35 in that two additional electron tubes are used to amplify the current of the plate circuit about twenty-five fold. It is then possible to replace the galvanometer by a sensitive milliammeter. The scale of the milliammeter may be calibrated directly in terms of $p_H$ units. Ingenious devices are provided for checking the calibration of the instrument, testing the performance of the individual electron tubes, etc.

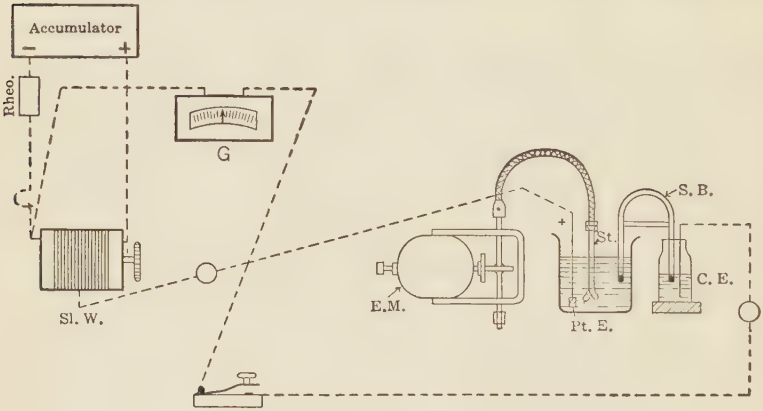

FIG. 36.—Simple monometallic system, balancing with slide wire.

| | | | |
|---|---|---|---|
| Rheo. | rheostat. | C. E., | calomel electrode. |
| Sl. W. | slide wire. | E. M. | motor for stirring. |
| Pt. E., | indicator electrode. | St., | stirrer. |
| S. B., | salt bridge. | G, | galvanometer. |

**6. General Remarks on the Performance of Potentiometric Titrations.**—One of the authors (Kolthoff) uses the arrangement illustrated in Fig. 36. By switching in the normal element (standard cell) NE and using the rheostat, *Rheo*, the E.M.F. from the accumulator can be adjusted at 2 volts. The sliding contact of the rotary bridge is put at a value 509.2, and the resistance in *Rheo* is regulated until the system is balanced. Since the E.M.F. of the standard cell is 1.0184 volt, we have:

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[18] Goode, K. H., J. Am. Chem. Soc., **47**, 2483 (1925).

$$\frac{509.2}{1000}E = 1.0184, \quad \text{or} \quad E = 2.$$

The standard cell has a small internal resistance and is easily polarized. Therefore, care should be taken that it does not deliver too strong a current. Before the cell is switched in, the resistance must be so regulated that the system is almost balanced. In order to be sure that the value found in this way is correct, the measurement should be repeated at the end of the titration. After this period of rest, the standard cell will again have its normal value.

The standard cell is switched out of the circuit, and the cell to be measured is introduced. Switches such as those described by W. M. Clark ("The Determination of Hydrogen Ions") have been found by the authors to be very convenient.

The various wires must be provided with good insulating material (e.g., rubber, etc.). An open glass beaker may usually be employed as a titration vessel. When it is necessary to exclude air, the titration vessel is provided with a rubber stopper with five holes: one for the siphon from the calomel electrode; one for the burette tip; another for the stirrer; and the remaining two for the introduction and escape of a stream of indifferent gas. *Cf.* Hostetter and Roberts [19] and W. T. Bovie [20] for other special vessels for this purpose.

In many cases the potential does not become constant immediately after the addition of reagent. The establishment of equilibrium may be hastened by stirring, and sometimes by heating. Many oxidation-reduction reactions are slow in attaining the equilibrium-potential near the equivalence-point. Heating to 60°–80° is usually a good means of shortening the titration time. One of the authors (Kolthoff) usually employs a micro burner placed under the titration vessel for the heating.

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[19] Hostetter and Roberts, J. Am. Chem. Soc., **41**, 1337 (1919).

[20] W. T. Bovie, J. Am. Chem. Soc., **44**, 2892 (1922).

Stirring the liquid during the titration diminishes the polarization effect. A motor-driven glass stirrer is usually the most effective means of stirring. A rheostat for the regulation of the speed of stirring should be provided. Kolthoff has often observed, especially in humid weather, that the motor ionized the air after a certain period of use, and the galvanometer then made random deflections although it was not switched into the circuit. In such instances, it is recommended that the motor be stopped during the potential measurements. In many cases, it is sufficient to bubble an indifferent gas through the solution instead of using an electric motor. Carbonic acid may be used for titrations in acid medium, while nitrogen or hydrogen should be employed for alkaline solutions.

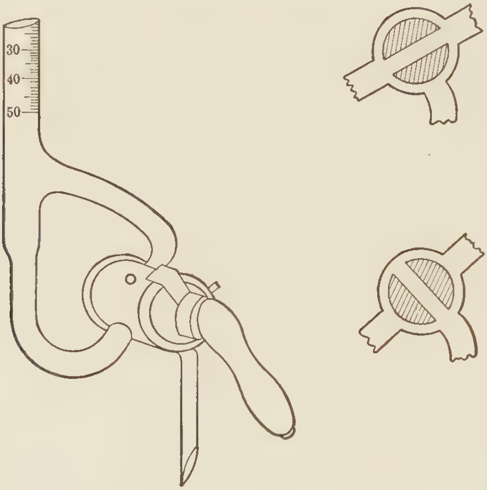

Fig. 37.—Drop-burette (Müller).

The reagent is introduced by means of a burette. For very accurate measurements, a weight burette should be used; an ordinary burette will serve in most cases. The burette is placed in such a way that when it is opened the liquid runs directly into the titration vessel. In the titration of warm liquids, the burette must be connected to a long glass tube which ends in the titration vessel, so that the burette is protected against temperature change during the titration and the readings are reliable. In the neighborhood of the equivalence-point, the reagent must be added drop by drop, as was mentioned in § 1 of this chapter. Erich Müller[21] has described several practical arrangements for measuring the drop volume, without danger of over-titrating while so doing. The drop volume is measured by taking 20–40 drops from the burette and reading the volume.

As stated above, the siphon between the calomel electrode vessel and the calomel electrode is usually filled with a saturated potassium chloride solution. When either the liquid to be titrated or the reagent reacts with chloride, potassium sulphate or nitrate, or ammonium nitrate should be used in the siphon. The shape of the electrode depends upon the nature of the titration. When metal electrodes are to be used, wires of pure metal may be taken, or the metal may be deposited on a Winkler gauze electrode. In the case of mercury, the latter method must be employed. For oxidation-reduction reactions, a bright platinum electrode should be used. A small platinum gauze (height about 1 cm.; diameter 3–5 mm.) is to be preferred to a small wire in most instances. Details regarding particular electrodes will be given in the section entitled "Special Determinations."

After each addition of reagent, the measurement is made by pressing the key which switches the galvanometer into circuit. *It is always necessary to repeat the measurement after stirring in order to be sure that the potential is constant. A further addition is not permissible until constancy is reached.* Only in this way can accurate results be obtained.

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[21] Erich Müller, Die Elektrometrische Massanalyse, 2d Ed., p. 65; Z. Elektro-Chem., **30**, 187 (1924).

## B.—SPECIAL DETERMINATIONS

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# CHAPTER IX

# PRECIPITATION AND COMPLEX-FORMATION REACTIONS, WITH METALLIC OR NON-METALLIC ELECTRODES

### 1. The Silver Electrode.—

$$p_{\mathrm{Ag}} = \frac{0.798 - E_H}{0.0591}. \quad \text{(At 25° C.)}$$

$E_H$ is the E.M.F. of the unknown electrode as related to the normal hydrogen electrode.

*Electrode.*—A piece of pure silver wire; a piece of silver melted into a capillary tube; or a platinum gauze electrode coated with silver electrolytically.

*Determination of Halides.*—R. Behrend [1] was the first to apply the silver electrode to the analytical titration of chloride, bromide, and iodide. He attained an accuracy of about 0.5 per cent. He also used the silver electrode for the separation of the different halides. His results will be discussed later.

A special study of the titration curve of silver with chloride in the presence of large amounts of salts has been made by W. D. Treadwell.[2] The salts change the shape of the curve to a marked degree, owing to complex-formation of the silver ions with the added salt. The end-point is found when an excess of silver is still present, at least when the reference electrode consists of a suspension of silver choride free from the salt (*cf.* p. 168). If, however, the reference electrode has the composition which the solution to be titrated will have at the equivalence-point, no error will result because of the complex-formation, and the repression of the dissociation (activity).

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[1] R. Behrend, Z. physik. Chem., **11**, 466 (1893).

[2] W. D. Treadwell, Helv. Chim. Acta, **2**, 672 (1919).

If we determine the position of the end-point by the general method $\left(\text{i.e., by the calculation of the maximum } \frac{\Delta E}{\Delta c}\right)$ the salt error will usually be negligible, in the opinion of the authors. Let us assume that the salt BA, which is added, forms the complex $BAAg^+$ with the silver ions; then we may write:

$$BA + Ag^+ \rightleftarrows BAAg^+,$$

and

$$\frac{[BA][Ag^+]}{[BAAg^+]} = K_{compl.}$$

$K_{compl.}$ is the complex constant. Since these complexes are not usually very stable, K will be rather large; the concentration of the salt added is also very large; therefore we may take BA in the equation as a constant. We then have:

$$\frac{[Ag^+]}{[BAAg^+]} = K'.$$

From this equation we see that at each silver-ion concentration a different part of the silver, but always the same relative part, is removed as complex ion. Hence the ratios of the silver-ion concentrations at different stages in the titration will be the same as those for the salt-free solution. Therefore the jump in potential will occur at the same place as in the salt-free solution. The complex-formation will cause an error of appreciable importance only in the titration of very dilute solutions of silver containing a high salt concentration.

An extended study of the titration of the halides with silver nitrate has been made by C. Liebich.[3]

*Chloride*: $S_{AgCl}$ = about $10^{-10}$.

According to Liebich, the potential very rapidly assumes a constant value in the titration of chloride with silver nitrate.

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[3] C. Liebich, Die Potentiometrische Bestimmung von Chlor, Brom, und Jod. Dissertation, Dresden (1920).

The titration yields accurate results even at dilutions of 0.001 N chloride. At greater dilutions good results are no longer obtained, partly because of the disturbing influence of the solubility of silver chloride. Addition of sulphuric acid to dilute solution has a favorable effect. The presence of an electrolyte such as barium nitrate or nitric acid is generally without influence on the result.

*Bromide*: $S_{AgBr} = 6.4 \times 10^{-13}$.

The potential is slow in assuming a constant value, especially in the vicinity of the equivalence-point. Hence, when the addition of silver nitrate is made too quickly, too much reagent is used (disadvantage of the Pinkhof system and its modifications). Near the equivalence-point the potential is constant after about five minutes' stirring. When Liebich titrated an 0.002 N bromide solution rapidly, 0.7 per cent too much silver nitrate was required, whereas the error was 0.35 per cent in slow titration. Even a 0.0001 N bromide solution may be titrated with an accuracy of 1 per cent; the disadvantage is that the titration requires a long time. Addition of sulphuric acid to dilute solutions again has a favorable effect, whereas the presence of barium nitrate or nitric acid has a disturbing influence.

*Iodide*: $S_{AgI} = 10^{-16}$.

Iodide may be titrated at very great dilutions with silver nitrate. This was shown by Dutoit and von Weisse[4] and has been confirmed by Liebich. A disadvantage is that a long period of time elapses before the potential is constant, in the equivalence-point region. No sharp maximum value of $\frac{\Delta E}{\Delta c}$ can be observed. The authors suppose that these defects are due to the strong adsorbing capacity of silver iodide for silver and iodide ions. According to Liebich, an improvement is made by the addition of sufficient barium nitrate (a concentration of about 5 per cent); the addition of sulphuric acid also has a favorable effect, but not as marked as that of the barium nitrate. In the titration of very dilute solutions it is necessary to wait a very long time before the potential is constant, even in the presence of barium nitrate; but under these conditions traces of iodide corresponding to a concentration of 10 parts per million can be determined with an accuracy of a few per cent.

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[4] P. Dutoit and von Weisse, J. chim. phys., **9**, 578 (1911).

*Application of the Müller System* (*Cf.* p. 150 ff.).—The application of the Müller system is not to be recommended when accurate results are desired. As we have seen, the potential does not become constant very rapidly; also, salts influence the equivalence-potential. Erich Müller [5] gives the following values for the "inflection potential" measured against the normal calomel electrode.

Chloride: $E_E = +0.24$ (calculated $+0.227$)

Bromide: $E_E = +0.18$ (calculated $+0.157$)

Iodide: $E_E = -0.04$ (calculated $+0.047$)

*Mixtures of Halides.*—Several investigations of the titration of the halides, in presence of each other, with silver nitrate, have been published. R. Behrend [6] developed a method for the titration of iodide in the presence of bromide. He stated that in neutral solutions part of the bromide was precipitated, together with the silver iodide; irregular potential values were observed. By the addition of a sufficient amount of ammonia he kept the bromide in solution and in this way determined only the iodide. After the first jump in potential was obtained he acidified the solution with nitric acid and titrated the bromide, or chloride. He did not succeed in titrating bromide in the presence of chloride. According to Dutoit and von Weisse [7] it is not necessary to use ammonia for the determination of iodide in the presence of bromide, at least when the concentration of the latter is no more than 50 times larger than the iodide concentration. Under other conditions the iodide may be precipitated as palladium iodide, thallium iodide, or cuprous iodide. The authors wish to remark, however, that iodide can not be separated from bromide in the form of cuprous iodide, since cuprous bromide is also slightly soluble. The precipitation of iodide as silver iodide in the presence of bromide or chloride in neutral solutions gives good results only when the solution is vigorously stirred during the titration.

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[5] Erich Müller, Die Elektrometrische Massanalyse, p. 88 and ff.

[6] R. Behrend, Z. physik. Chem., **11**, 466 (1893).

[7] Dutoit and von Weisse, J. chim. phys., **9**, 578 (1911).

Pinkhof[8] has confirmed the fact that iodide may be determined as described by Dutoit and von Weisse. At a bromide concentration of 0.1 N, no silver bromide is precipitated as long as the iodide concentration is greater than $10^{-4}$ N, corresponding to a silver-ion concentration of $10^{-12}$. Hence, Pinkhof, in his simple system, uses a reference electrode with the silver-ion concentration which is given by a suspension of silver bromide in 1 N potassium bromide. The end-point is observed at an iodide concentration of $10^{-4}$ N. From this it is evident that an accurate determination of a small amount of iodide in the presence of a large excess of bromide is not possible by the above method.

None of the investigators mentioned succeeded in titrating bromide in the presence of chloride in neutral solution. Following the lead of Behrend, Pinkhof tried to prevent the precipitation of silver chloride by the addition of ammonium carbonate. Silver chloride is completely soluble in 0.5 N ammonium carbonate, and silver bromide, which is precipitated from this solution, does not carry down silver chloride. The bromide is precipitated until the bromide concentration is as low as $3 \times 10^{-4}$. Therefore, Pinkhof fixed the equivalence-potential at a bromide concentration of $10^{-3}$ N, with a silver-ion concentration of $6 \times 10^{-10}$. As a reference electrode he uses a suspension of silver chloride in 0.2 N potassium chloride. A bromide-ion concentration of $10^{-3}$ N is added to the result. The accuracy of the titration is about 1 per cent when the chloride concentration is no more than 10 times the bromide concentration. For the authors' objections to this system, *cf.* p. 151ff.

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[8] Pinkhof, Over de Toepassing der Elektrometrische Titraties, Dissertation, Amsterdam (1919), p. 17.

C. Liebich (*loc. cit.; cf.* also Schindler, *loc. cit.*) was unable to determine iodide accurately in the presence of bromide. Even when he titrated very slowly, he found 2 to 4 per cent too much iodide. An improvement consisted in the addition of 5 per cent of barium nitrate, whereupon accurate results were obtained. In the titration of iodide in the presence of chloride, about 5 per cent too much iodide, and too little chloride, is found. In the titration of bromide in the presence of chloride, about 8 to 10 per cent too much silver is used before the first jump in potential occurs. The errors are caused by the formation of solid solutions of the various halides, as has been described by F. W. Küster[9] and A. Thiel.[10] According to Liebich, the addition of barium nitrate or alum seems to prevent the mixed halide precipitation, even in the case of silver bromide and chloride. The addition of the salts mentioned has the same effect as the addition of ammonium carbonate, which Pinkhof proposed. The accuracy, however, is never greater than 1 per cent; and when the ratio of $Cl^-$ to $Br^-$ is larger than 1 : 10, good results are no longer obtained. When the ratio is 1 : 30 the jump in potential no longer occurs. In the opinion of the authors, this is explained by the small ratio between the solubility products of silver chloride and silver bromide. It is a very peculiar fact that in the titration of mixed halides the potential becomes constant much sooner than in the determination of the individual halides.

To summarize: Iodide may be determined in the presence of bromide or chloride or both, with silver nitrate, when the solution contains about 5 per cent of barium nitrate. The accuracy is 0.5 to 1 per cent.

Inaccurate results are obtained in the titration of bromide in the presence of chloride with silver nitrate. When the ratio $Cl^-$ to $Br^-$ is not greater than 10, approximate values are obtained for the bromide content when the solution is 0.5 N with respect to ammonium carbonate (Pinkhof) or when 5 per cent barium nitrate is present. The authors can not recommend the method for accurate determinations.

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[9] F. W. Küster, Z. anorg. Chem., **19**, 81 (1899).

[10] A. Thiel, Z. anorg. Chem., **24**, 1 (1900)

*Thiocyanate:* $S_{AgCNS} = 2 \times 10^{-12}$.

According to Behrend *(loc. cit.)* and Kolthoff's experience, thiocyanate may be accurately titrated with silver nitrate, or the reverse. The error due to adsorption may be prevented by the addition of 1 per cent barium nitrate.[11] According to Müller, $E_E = +0.108$ volt (against normal calomel electrode; calculated 0.161 volt). Since silver bromide and silver thiocyanate both have about the same solubility, they are precipitated together upon titration with silver.

In the titration of thiocynate in the presence of chloride, we encounter the same difficulties as in the case of the chloride and bromide. Addition of barium nitrate improves the results.

*Ferrocyanide.*[12]—Two jumps in potential are obtained, one at a point which corresponds to the formation of $KAg_3Fe(CN)_6$; the second to $Ag_4Fe(CN)_6$. The titration does not give accurate results, since the maximum value of $\frac{\Delta E}{\Delta c}$ is not sharply defined.

*Cyanide:*

$$\frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} = \text{about } 10^{-21}.$$

$$^{13}[Ag^+][Ag(CN)_2^-] = 5 \times 10^{-12}.$$

*Cf.* p. 101 on the theory of this titration.

In the titration of a cyanide solution with silver nitrate, the cyanide first forms the complexion $Ag(CN)_2^-$. After the quantitative occurrence of this reaction there is a jump in the potential, after which the silver cyanide (this name will be used instead of silver silvercyanide, $Ag[Ag(CN)_2]$) is precipitated. W. D. Treadwell [14] was the first to apply this reaction for the determination of cyanide in the presence of ferrocyanide. Later, Erich Müller and H. Lauterbach [15] made a more extended study of this titration. From their results the authors conclude that the first jump in potential occurs 0.5 to 1 per cent too early, or the second break too late by the same percentage. Müller and Lauterbach do not discuss this question; the authors wish to note that from an analytical point of view it is of great importance to know the absolute accuracy of this titration method.

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[11] *Cf.* Erich Müller, *loc. cit.*, p. 111; Rudolph, Dissertation, Dresden (1922).

[12] Niemz, Potentiometrische Titrationen von Blei und Silber mit Ferrocyankalium, Dissertation, Dresden (1920).

[13] Bodländer and Lucasse, Z. anorg. Chem., **41**, 192 (1904).

[14] W. D. Treadwell, Z. anorg. Chem., **71**, 223 (1911).

When the solution contains iodide, the first jump in potential occurs at the point where the complex ion is formed, after which silver iodide begins to be precipitated. After this precipitation is complete there is a second jump in potential, whereupon silver cyanide begins to be precipitated. At the completion of the iodide precipitation a third break in the potential occurs. From the results obtained by Müller and Lauterbach, the authors conclude that the accuracy is not higher than 1 to 2 per cent. In the presence of bromide or chloride only two jumps in potential are found, one at the end of the complex silver-cyanide-ion formation, the other at the completion of the precipitation of silver cyanide, bromide, and chloride. We should not expect a third break in the potential in this case, since the solubility product of silver cyanide is about the same as that of silver bromide. (Thiocyanate behaves in the same fashion as bromide.)

From the foregoing it is evident that we have an easy means of making an analysis of a mixture of cyanide, iodide, and bromide (or chloride and thiocyanate).

In a pure cyanide solution the amount of reagent which we require to reach the first jump in potential is the same as that from the first to the second break. In the presence of iodide, the amount of reagent added between the first and the second jump corresponds to the iodide content. (See Fig. 38.)

In the presence of the other halogens, we have the following conditions:

Used to reach the first jump in potential *a* cc. reagent.

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[15] E. Müller and H. Lauterbach, Z. anorg. Chem., **121**, 178 (1922).

Used from first to second jump in potential *b* cc. reagent.
Used from second to third jump in potential *c* cc. reagent.

Then we have:

*a* corresponds to the cyanide content;
*b* corresponds to the iodide content;
(*c–a*) corresponds to the sum of Br, Cl, CNS.

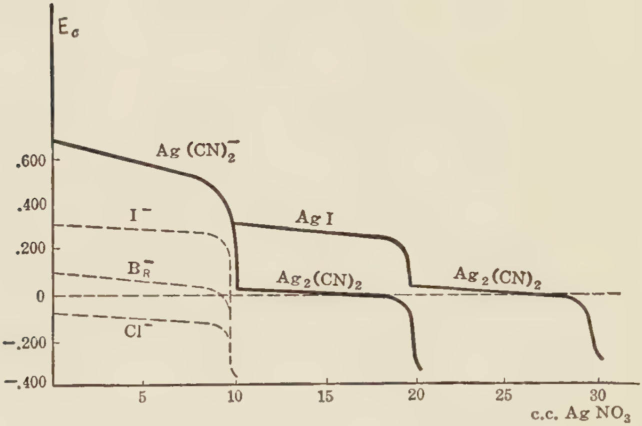

FIG. 38.—Titration curve of cyanide.

In order to accelerate the titration, Müller and Lauterbach recommend the Müller modification of the Pinkhof system. The equivalence-potentials are given in the following table.

EQUIVALENCE-POTENTIALS AGAINST NORMAL CALOMEL ELECTRODE, ACCORDING TO MÜLLER AND LAUTERBACH

| Solution to be Titrated | First Jump, ($Ag(CN)_2^-$) | Second Jump | Third Jump |
|---|---|---|---|
| $CN^-$ alone | −0.134 | +0.106$Ag[Ag(CN)_2]$ | |
| $CN^-$ $I^-$ | −0.32 | −0.08(AgI) | +0.21$Ag[Ag(CN)_2]$ |
| $CN^-$ $Br^-$ | −0.214 | +0.20 | |
| $CN^-$ $Cl^-$ | −0.18 | +0.25 | |
| $CN^-$ $I^-$ $Br^-$ | −0.33 | −0.134(AgI) | +0.20 |
| $CN^-$ $I^-$ $Cl^-$ | −0.35 | −0.107(AgI) | +0.23 |
| $CN^-$ $Br^-$ $Cl^-$ | −0.18 | +0.25 | |

It should be recalled here that these values are not absolute values of the equivalence-potential, but depend upon the ratios of the substances to be titrated. In unknown cases the authors recommend the general method in which $\frac{\Delta E}{\Delta c}$ is determined.

*Practical Applications of the Cyanide Titration.—Determination of Silver Halides in Photographic Films and Dry Emulsions.*[16]—If we have silver iodide, for example, which we dissolve in an excess of potassium cyanide, the following reaction takes place.

$$AgI + 2CN^- \rightleftarrows Ag(CN)_2^- + I^-.$$

Now if we add silver nitrate to the solution the excess of cyanide is first transformed into the complex cyanide ion, whereupon a jump in the potential occurs; the silver iodide then begins to be precipitated. The amount of reagent that is used between the first and second potential jumps corresponds to the silver-iodide content. The advantage of this method is that we do not need to know the strength and the excess of the cyanide solution in which we dissolve the silver iodide. Nor do we need to know the strength of the cyanide solution in the determination of silver chloride or bromide, although the silver cyanide is precipitated together with the other silver halides after the first potential break.

During the titration with silver nitrate, the excess of free cyanide is first transformed into the complex $Ag(CN)_2^-$. After this point has been reached, a like amount of reagent is required to precipitate the complex ion as silver cyanide. The amount of silver nitrate required to precipitate the complex which is formed by the solution of the silver halide and the bromide is equal to twice the amount of silver bromide present:

$$2CN^- + AgBr \rightleftarrows Ag(CN)_2^- + Br^-,$$

since the solution contains equivalent amounts of complex and bromide ions. Hence, if the amount of silver nitrate used from the beginning up to the first potential jump is $a$ cc. 0.1 N, and if that used from the first to the second jump is $c$ cc. 0.1 N, then the amount of AgBr is equal to $\frac{c - a}{2} \cdot \frac{1}{10}$ millimoles.

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[16] Erich Müller (R. Hartmann and R. Troppisch) Die Photograph Industrie, Nos. 18 and 19 (1924).

If we have a mixture of silver iodide and silver bromide or chloride, there are three potential breaks upon titrating back with silver nitrate. If $a$ cc. are used to the first, $b$ from the first to the second, and $c$ from the second to the third, then $b$ corresponds to the amount of iodide present. Equivalent amounts of complex and iodide ions are formed upon solution of the silver iodide in the cyanide. We precipitate the complex together with the silver bromide. Hence the amount of silver bromide corresponds to:

$$\frac{c - a - b}{2}.$$

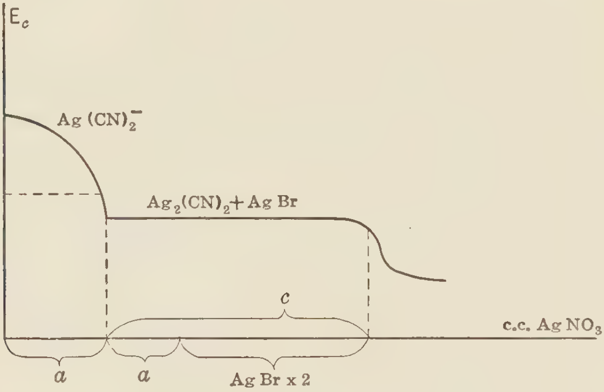

FIG. 39.—Titration curve of cyanide and bromide with silver nitrate.

Hence, in all of these instances, we do not need to know the strength of the cyanide solution. If the silver halides contain alkali halides as well, we may determine the latter at the same time; but in this case we must know the strength of the cyanide solution.

If the ratio between silver iodide and bromide is not favorable, it is not practicable to determine both in one sample of material. If, for example, the amount of silver iodide is very small in comparison with the amount of silver bromide, there is but little reagent used between the first and second potential breaks, unless a large amount of the substance be taken for the determination. We should then need a very large amount of silver solution for the estimation of the bromide. Therefore, it is better to make two determinations: one with a large amount of substance in order to use sufficient silver nitrate for the accurate titration of the iodide; the other with a suitable amount of substance for the determination of the silver bromide. We encounter the conditions just mentioned in the titration of silver halides in films and dry emulsions (ratio AgI : AgBr, about 1 : 30).

In this instance we have the difficulty that the gelatine, which also dissolves in the cyanide solution, has a disturbing influence on the jump in potential (complex silver-protein compounds); therefore no sharp maximum value of $\frac{\Delta E}{\Delta c}$ can be observed, and the titration does not give accurate results. In order to prevent, as far as possible, the solution of the gelatine, Erich Müller recommends the extraction of the films by a cold cyanide solution with constant stirring (five to ten minutes) and filtration. But the extraction of the silver halides from dry emulsions is incomplete in this way. These emulsions must be shaken with water at 40° C. until the gelatine is dissolved; after cooling, an excess of cyanide is added.

In order to diminish the disturbing action of the gelatine, the solution is strongly diluted and sodium carbonate (free from chloride) is added. From the data which Müller gives, however, it may be concluded that the maximum value of $\frac{\Delta E}{\Delta c}$ is not sharply pronounced and that accurate results are not obtained. Therefore the authors recommend that the gelatine be destroyed, although this procedure complicates the analysis. By heating the emulsion with sufficient dry sodium carbonate the gelatine is burned, and the residue contains the halides in water-soluble form. Either the halides may be extracted and titrated with silver nitrate (*cf.* p. 164), or the silver carbonate may be dissolved in acid and titrated, or the whole may be treated with an excess of cyanide.

*Application of the Cyanide Method to the Determination of Nickel.*—An ammoniacal nickel solution reacts with cyanide to form a complex nickel cyanide ion:

$$Ni(NH_3)_6Cl_2 + 4KCN \rightleftarrows 6NH_3 + 2KCl + K_2Ni(CN)_4$$

or

$$Ni^{++} + 4CN^- \rightleftarrows Ni(CN)_4^=.$$

A number of years ago, Moore[17] applied this reaction to the titration of nickel with cyanide, potassium iodide being used as indicator in the titration of the excess of cyanide with silver nitrate. As long as there is an excess of cyanide the solution remains clear. E. Müller and H. Lauterbach[18] adapted this method to potentiometric titration. An excess of potassium cyanide is added so that the nickel solution is colorless. The excess of cyanide is titrated with silver nitrate. A potential jump takes place when the free cyanide has been transformed into the complex silver cyanide. At this point the nickel is present as the complex $Ni(CN)_4^=$. If the total amount of cyanide added is known, and the excess has been determined in this manner, the nickel content may be calculated, since 1Ni is equivalent to 4CN. The authors conclude from the results of Müller and Lauterbach that this method does not yield exact results. The jump in potential is very small in ammoniacal solution, and if the titration is made in neutral solution other difficulties occur.

The modified Pinkhof system may be used by titrating to an inflection potential of $-0.212$ volt (against normal calomel electrode). In a recent publication E. Müller and W. Schluttig[19] observed that the silver electrode is a direct indicator for cyanide ions. They attempted to titrate a nickel solution directly with a standardized potassium cyanide solution. The following are the reactions:

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[17] Moore, Chem. News, **72**, 92 (1895).

[18] E. Müller and H. Lauterbach, Z. analyt. Chem., **61**, 457 (1922).

[19] E. Müller and W. Schluttig, Z. anorg. Chem., **134**, 327 (1924).

$$Ni^{++} + 2CN^{-} \rightleftarrows Ni(CN)_2,$$
$$Ni(CN)_2 + 2CN^{-} \rightleftarrows Ni(CN)_4^{=}.$$

They only found a break in potential at the point that corresponds to the complex ion; the end-point was found too soon (error about 7 per cent). This error is due to the precipitation of nickel cyanide which reacts slowly with the excess of cyanide. This error may be avoided by titrating very rapidly and by opposing an inflection-potential of $-0.253$ volt to that of the cell (against normal calomel electrode). The titration may be finished in about two minutes; constant and effective stirring is necessary. There is great danger of over-titrating. In principle, it is better to apply the reverse titration, i.e., to add the nickel solution to a known amount of cyanide. In this case there is no danger of precipitating nickel cyanide. Inflection potential $-0.15$ to $-0.17$ volt.

*Application of the Cyanide Method to the Determination of Cobalt.*—With cyanide, cobalt forms $Co(CN)_2$ which dissolves in an excess of cyanide to form $Co(CN)_6^{----}$. If, however, an excess of cyanide is added to a cobalt solution and titrated back with silver nitrate, the potential break occurs at a point corresponding to $Co(CN)_5^{=}$.[20] E. Müller and H. Lauterbach[21] have studied this potentiometric titration. In the absence of ammonia the method gives accurate results; the inflection-potential lies at $-$ 0.29 to $-$ 0.30 volt (against normal calomel electrode). E. Müller and W. Schluttig[22] tried the direct titration, using the silver electrode as indicator. They met the difficulty that the complex cobalt cyanide ion was rapidly oxidized to the cobalti- form by the oxygen of the air. It was therefore necessary to work in a hydrogen atmosphere. For various reasons, which will not be discussed here, inaccurate results were obtained in the direct titration of cobalt with cyanide. In the reverse titration two maxima in $\frac{\Delta E}{\Delta c}$ are found very close together. The first corresponds to the formation of the complex $Co(CN)_5^{\equiv}$, the second to $Co(CN)_4^{=}$:

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[20] Rupp and Pfenning, Chem. Ztg., **34**, 322 (1910); F. Edelmann, Dissertation, Dresden (1915).

[21] E. Müller and H. Lauterbach, Z. analyt. Chem., **62**, 23 (1923).

[22] E. Müller and W. Schluttig, Z. anorg. Chem., **134**, 327 (1924).

$$4Co(CN)_5^{\equiv} + Co^{++} \rightleftarrows 5Co(CN)_4^{=}.$$

In the absence of air the first jump is very sharp and an accurate determination is obtained by working in a hydrogen atmosphere. Twenty-five cubic centimeters of 0.1 N potassium cyanide solution are diluted to 100 cc.; a silver electrode is immersed in the solution, hydrogen is passed through, and the solution is stirred. The titration is carried to an inflection-potential of $-0.49$ (against normal calomel electrode). 1CN corresponds to $\frac{1}{5}$Co.

*Application of the Cyanide Method to the Determination of Zinc.*—Zinc cyanide is soluble in an excess of potassium cyanide with the formation of the complex $Zn(CN)_4^{=}$ ion. E. Müller and Adam [23] add a known excess of cyanide to a neutral zinc solution, and titrate the excess with silver nitrate, using a silver wire as indicator electrode. There is no break in potential at the point where the zinc is transformed into complex ion, because the stability of this complex is very small. The zinc complex reacts with more silver nitrate to form zinc cyanide and the complex silver cyanide:

$$Zn(CN)_4^{=} + Ag^{+} \rightleftarrows Ag(CN)_2^{-} + Zn(CN)_2.$$

There is a rather distinct potential jump when all of the zinc cyanide has been precipitated. Inflection-potential $-0.185$ volt (against normal calomel electrode). On continued addition of silver nitrate there is a second marked change in potential when all of the silver complex is precipitated. The zinc content may be calculated from the amounts of reagent corresponding to these two points. It is not necessary to know the strength of the cyanide if that of the silver nitrate is known. 1CN corresponds to $\frac{1}{2}$Zn. One of the authors (Kolthoff) obtained good results when the concentration of zinc was larger than 0.005 molar. The error was −0.2 to −0.75 per cent zinc. In more dilute solutions the error was greatly increased because of the hydrolysis of the zinc cyanide. Cadmium, lead, and copper have a disturbing action. It is possible, however, to determine silver and zinc successively when they are present in the same solution.

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[23] E. Müller and Adam, Z. Elektrochem., **29**, 49 (1923).

*Phosphate and Arsenate.*—Neither Pinkhof (*loc. cit.*, 1919) nor W. D. Treadwell and L. Weiss [24] succeeded in the potentiometric titration of phosphate and arsenate with silver nitrate. In the opinion of the authors, the difficulty lies in keeping the hydrogen-ion concentration low enough to keep the solubility of the silver precipitate low. They suggest that the addition of a suitable buffer, possibly sodium bicarbonate, will have a favorable effect.

*Sulphide.*—P. Dutoit and von Weisse [25] applied their polarized system to the potentiometric titration of silver with sulphide, and the reverse. From their data it may be concluded that the determination gives very unsatisfactory results; errors of 10 per cent or more occur. In very dilute solution, three times as much as the calculated amount of sulphide was needed before the jump on potential was found. The errors are probably due mainly to the polarized system. Treadwell and Weiss (*loc. cit.*) were successful in the determination of hydrogen sulphide in a dilute solution with silver nitrate. As a reference electrode they used silver in contact with silver sulphide suspended in dilute sodium nitrate.

H. H. Willard and F. Fenwick [26] used the bimetallic electrode system (*cf.* p. 153); ammoniacal silver nitrate was used as a reagent (0.05 N silver nitrate containing 30 cc. of 28 per cent ammonia per liter). Accurate results were obtained. Willard and Fenwick investigated the influence of the more common impurities in alkali sulphide. Chloride, sulphite, and sulphate did not interfere with the sharpness of the end-point, although in all of these cases slightly less than the theoretical amount of reagent was required. The error was greatest in the presence of chloride. Thiosulphate rendered the potential change less distinct, but did not seriously affect the clarity of the end-point. The thiosulphate caused a slight decrease in the amount of reagent required (0.07 cc. of 0.05 N silver nitrate). In polysulphides, only the normal sulphide is titrated with silver nitrate. The method was also applied to the determination of sulphur in steel.

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[24] W. D. Treadwell and L. Weiss, Helv. Chim. Acta., **2**, 680 (1919).

[25] P. Dutoit and von Weisse, J. chim. phys., **9**, 630 (1911).

[26] Willard and Fenwick, J. Am. Chem. Soc., **45**, 645 (1923).

In the authors' opinion,[27] the titration of sulphide with silver nitrate gives good results, especially when the sulphide solution is more concentrated than 0.02 N. The potential is constant very soon after the addition of the reagent; therefore the simple Müller method may be advantageously applied. Inflection-potential, according to Kolthoff and Verzijl, −0.400 volt (normal calomel cell). Erroneous results were obtained in the titration of very dilute solutions; too little reagent is used at the potential break. In the titration of 0.0001 N sulphide solutions, the error was 8 to 10 per cent. (In this case the titration with mercuric chloride is better. *Cf.* p. 191.)

*Thiosulphate.*—There are two jumps of potential in the titration of thiosulphate with silver nitrate, according to Erich Müller.[28]

The first, at the completion of the reaction:

$$S_2O_3^{=} + Ag^+ \rightleftarrows AgS_2O_3^-,$$

is very small. The second is larger and is found at the completion of the precipitation of silver thiosulphate:

$$S_2O_3^{=} + 2Ag^+ \rightleftarrows Ag_2S_2O_3.$$

This second maximum value of $\frac{\Delta E}{\Delta c}$ occurs too late, because of the decomposition of the silver thiosulphate:

$$Ag_2S_2O_3 + H_2O \rightleftarrows Ag_2S + H_2SO_4.$$

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[27] I. M. Kolthoff and E. J. A. Verzijl, Rec. trav. chim., **42**, 1055 (1923).

[28] Erich Müller, Z. anorg. Chem., **134**, 201 (1924).

This decomposition can be observed after the complex has been formed. A greater amount of silver nitrate gives brown silver sulphide. The latter has a strong absorbing capacity, which causes the error. The enormous effect of temperature is noteworthy. If the titration is carried out at 18° C., the second maximum occurs 11 per cent too late; but at 0° C. it appears at the theoretical point. In the reverse titration the dark-colored silver sulphide is formed at the start of the titration. The addition of a sufficient amount of sodium acetate obviates this difficulty, and the titration gives a sharp end-point at all temperatures. The titration may be performed especially rapidly at 70°–80° C. In the authors' opinion, this thiosulphate titration is of more theoretical than practical significance.

*Titration of Silver.*—Any of the various anions that may be titrated with silver nitrate might be used for the determination of silver. We are limited in our choice, however, as the reagent must be stable, and must give a sharp and accurate end-point. Sulphide and cyanide can not be recommended as reagents because their solutions deteriorate rapidly; in special instances they may be of service. Of the halides, iodide and bromide do not give accurate results in the more concentrated solutions. The maximum value of $\frac{\Delta E}{\Delta c}$ is not very pronounced, probably because of the strong adsorbing power of the silver halides. Addition of barium nitrate improves the determinations. Potassium or sodium chloride gives the best results as reagent for the more concentrated silver solutions. Inflection-potential, about + 0.25 volt (normal calomel electrode).

F. Fenwick [29] uses the bimetallic electrode system, consisting of two fine thermocouple wires (wound in a loose spiral) polarized with current at 0.5 volt through an external resistance of 100,000 ohms. According to her experience, the break at the end-point decreases in magnitude as the solubility of the silver salt increases, and is therefore poorest in the titration of chloride.

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[29] Florence Fenwick, The Theory and Application of Bimetallic Electrode Systems in Electrometric Analysis, Dissertation, Ann Arbor, Mich. (1923), p. 60. (*Cf.* § 4, Chapter VIII, p. 153.)

The end-point is a slight rise followed by a slow fall in potential difference between the two electrodes. "The change is not as abrupt as in many cases, but is perfectly distinguishable, especially after a little practice. Due to the very weak oxidizing potential of the solution to be titrated, the initial voltage is high and there is little change up to the immediate vicinity of the end-point. The electrodes should not be cleaned between titrations, as the inversion point increases in clarity with the first few successive titrations." The titration of silver with chloride, or the reverse, may be made with an accuracy of 0.1 per cent.

It is of theoretical importance to note that the ordinary titration of silver with chloride or other anions need not be carried out with a silver electrode, as the jump in potential also occurs if a platinum, palladium, gold, or mercury electrode is used.[30] The potentials are more noble than those of the silver electrode. Probably the noble metals are covered electrolytically with a thin layer of metallic silver.

The authors recommend the silver electrode for practical use.

According to W. D. Treadwell, S. Janett, and W. Blumenthal,[31] protective colloids, such as starch, gum arabic, and other colloidal carbohydrates, decrease the sharpness of the jump in potential, since they apparently increase the solubility of the silver halide. Fortunately, however, they have not much influence on the accuracy of the titration. This is no longer the case when proteins are present. These substances may combine with silver ions to form complex ions or "adsorption compounds."[32] Under unfavorable conditions the colloidal matter must be destroyed before the silver titration can be carried out.

The potentiometric method is of great importance in the investigation of the state of silver in the colloidal silver preparations which are used in medicine. There are at present more than two hundred of these preparations, in which the silver-ion concentration may be determined by potentiometric measurement.[33] According to Treadwell, Janett, and Blumenthal (*loc. cit.*), the iogenic silver may be determined by potentiometric titration, but they do not give the experimental details. I. M. Kolthoff and O. Tomicek[34] made an extensive study of the titration of silver in protargol (argenti proteinatum) and collargol (colloid silver; argentum Crédê). All of the silver of protargol may be transformed into silver halide by treatment with halide solutions. The silver halides that are formed remain in collodial solution because of the presence of protective colloids, so that one has the impression that no action has taken place. We may conclude from the change in potential, however, that the silver halides are formed. The best results are obtained by titration of the acidified protargol solution with iodide. In this instance two jumps in the potential are found, one after the transformation of all of the silver proteinate into silver iodide:

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[30] Erich Müller, Z. Elektrochem., **30**, 419 (1924).

[31] W. D. Treadwell, S. Janett, and W. Blumenthal, Helv. Chim. Acta, **6**, 513 (1923).

[32] F. Röhmann and L. Hirschstein, Beitr. Chem. physiol. pathol., **3**, 288 (1903); G. Galeotti, Z. physiol. Chem., **42**, 330 (1904); F. Liebert, Chem. Weekblad, **21**, 167 (1924); I. M. Kolthoff and O. Tomicek, Chem. Weekblad, **21**, 106 (1924).

$$\text{AgProt.} + \text{I}^- \rightleftarrows \text{AgI} + \text{Prot.}^-,$$

and the other after the transformation of the silver chloride, which occurs in all commercial preparations, into silver iodide:

$$\text{AgCl} + \text{I}^- \rightleftarrows \text{AgI} + \text{Cl}^-.$$

Hence it is possible, by one simple titration, to determine both the total silver content and the amount that is present as silver chloride.

In the following table the authors give an example in which a solution of 0.5g. protargol in 100 cc. water and 10 cc. 4 N sulphuric acid was titrated with 0.01N KI.

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[33] Th. Paul, Z. Elektrochem., **18**, 521 (1912); H. Seller and W. Thiessenhusen, Z. angew. Chem., **37**, 837, 855 (1924).

[34] I. M. Kolthoff and O. Tomicek, Rec. trav. Chem. **44**, 103 (1925); *cf.* also Kolthoff, J. Am. Pharm. Assoc., **14**, 183 (1925); R. B. Smith and P. M. Giesy, J. Am. Pharm. Assoc., **14**, 10 (1925).

| Cubic Centimeters of Reagent | E (*vs.* N-calomel electrode) | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|
| 0 | 0.372 | |
| 20 | 0.346 | |
| 29 | 0.296 | |
| 30 | 0.290 | |
| 31 | 0.278 | |
| 32 | 0.258 | 20 |
| 32.5 | 0.240 | *36* (First maximum: |
| 33.0 | 0.222 | *36* AgProt → AgI) |
| 34 | 0.218 | 4 |
| 36 | 0.154 | 32 |
| 36.6 | −0.036 | *330* (AgCl → AgI) |
| 37 | −0.094 | 140 |
| 38 | −0.118 | 24 |
| 40 | −0.142 | |

First maximum: 32.75 cc. 0.01 N $I^-$, corresponding to 7.08 per cent silver proteinate (present 7.08 per cent).

Second maximum: (36.6 − 32.75) 3.85 cc. 0.01 N $I^-$ corresponding to 0.83 per cent silver chloride (present 0.79 per cent).

The maxima are less pronounced in neutral solution.

*Determination of Formaldehyde.*—The potentiometric silver titration may be applied to the determination of formaldehyde. Erich Müller[35] adds an excess of silver nitrate and sodium carbonate to the solution to be titrated, and, after waiting five minutes, titrates back with potassium chloride:

$$HCOH + 2Ag^+ + H_2O \rightarrow HCOOH + 2H^+ + 2Ag.$$

This method is not at present of much practical importance. The direct titration of formaldehyde with silver solution was not found possible.

### 2. The Mercury Electrode.

$$p_{Hg_2} = \frac{0.750 - E_H}{0.0591} \quad (25° \text{ C.}).$$

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[35] Erich Müller, and W. Löw, Z. analyt. Chem., **64**, 297 (1924).

*Electrode.*—Platinum gauze, electrolytically coated with mercury. After a period of use, the electrode must be coated anew with mercury.

*General Remarks.*—When a solution containing mercurous and mercuric ions is in contact with mercury, an equilibrium is established, as represented by the equation:

$$\mathrm{Hg} + \mathrm{Hg}^{++} \rightleftarrows \mathrm{Hg_2}^{++}.$$

The mercuric ions are reduced; in the above equation we may regard the concentration of mercury as constant, and write the Mass Law expression:

$$\frac{[\mathrm{Hg_2}^{++}]}{[\mathrm{Hg}^{++}]} = \mathrm{K}.$$

According to Ogg,[36] K is equal to 235. In agreement with this value, Abel[37] found 235.5.

The following conclusions may be drawn:

(*a*) A mercurous salt solution can never be made quite free of mercuric ions by treatment with mercury, since $\frac{1}{235}$ of the mercury will remain in the mercuric form.

(*b*) When a mercuric solution is in contact with a mercury electrode, reduction will take place until the ratio between the mercuric and mercurous ions is equal to 235. From the data given in the literature we may calculate that a mercuric chloride solution will be practically completely reduced to calomel by treatment with mercury. Since the mercury electrode has a small surface, the reaction is slow, and therefore it might be possible to titrate a chloride solution with a mercuric salt (*cf.* below). The difficulty is not caused by the reduction, which has no effect on the analytical accuracy:

$$\mathrm{HgCl_2} + \mathrm{Hg} \rightleftarrows \mathrm{Hg_2Cl_2}.$$

From the analytical point of view, the form in which the transformed chloride is present is indifferent, since the same amount of reagent is used in either case.

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[36] Ogg, Z. physik. Chem., **27**, 285 (1898).

[37] Abel, Z. anorg. Chem., **26**, 376 (1901).

A practical objection to such titrations might be that, owing to the electrode reactions, the potential will be variable.

*Reagents:*

*Mercurous Solutions:* (*a*) *Mercurous Nitrate.*—0.1 N solution; salt dissolved with the aid of a little nitric acid; may be kept for a long time.

(*b*) *Mercurous Perchlorate.*—According to F. Fenwick [38] this salt may be readily obtained in a pure state; it is stable and does not give a precipitate on dilution. The 0.1 N solution is made by dissolving 10.83 g. of pure mercuric oxide in 10 g. perchloric acid, heating over metallic mercury, and diluting to 1 liter.

*Mercuric Solutions: Mercuric Nitrate.*—Commercial C. P. preparations are dissolved in water with the aid of a little nitric acid.

*Mercuric Perchlorate.*—This salt may be obtained in a pure, crystallized water-soluble form, which gives no precipitate of basic salt. A solution of the salt may be obtained by shaking a small excess of mercuric oxide with perchloric acid solution, until the liquid is saturated with the oxide. After filtration the solution is diluted to the proper volume.[39]

*Mercuric Chloride.*—As we shall see later, it is sometimes advantageous to use mercuric chloride as a reagent, although it is slightly dissociated. The pure salt is readily obtained by recrystallization from water.

*Halides.*—R. Behrend [40] was the first to apply the mercury electrode to the titration of halides. In agreement with his statements, W. D. Treadwell and L. Weiss,[41] and I. M. Kolthoff and E. J. A. Verzijl [42] found that chloride and bromide can be titrated accurately with mercurous nitrate as a reagent.

$$S_{Hg_2Cl_2} : [Hg_2{}^{++}][Cl^-]^2 = 3.5 \times 10^{-18},$$

$$S_{Hg_2Br_2} : [Hg_2{}^{++}][Br^-]^2 = 1.3 \times 10^{-21}.$$

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[38] F. Fenwick, Dissertation, Ann Arbor, Mich., 1922, p. 79.

[39] I. M. Kolthoff, Die Konduktometrischen Titrationen, Dresden (1923), p. 65.

[40] R. Behrend, Z. physik. Chem., **11**, 466 (1893).

[41] W. D. Treadwell and L. Weiss, Helv. Chim. Acta, **2**, 691 (1919).

[42] I. M. Kolthoff and E. J. A. Verzijl, Rec. trav. chim., **42**, 1056 (1923).

Erich Müller and H. Aarflot[43] prefer the use of mercurous perchlorate, and titrate to an inflection-potential of + 0.32, or for bromide to + 0.29 volt (against normal calomel electrode). According to their findings, chloride may be titrated with mercuric perchlorate; inflection-potential, + 0.41 volt. The titration of a mixture of mercurous and mercuric mercury with chloride did not give two separate jumps in potential.

It is not possible to make a separate titration of bromide in the presence of chloride with mercurous salt as reagent. The titration curve of iodide with mercurous salt is very peculiar. The solubility product is:

$$[Hg_2^{++}][I^-]^2 = 1.2 \times 10^{-28};$$

hence we should expect a sharp rise in the potential at the equivalence-point. In the titration of iodide with mercurous perchlorate, Müller and Aarflot found that too little reagent was required, the error being 0.5 to 2 per cent. The yellow mercurous iodide is decomposed in the beginning of the titration:

$$Hg_2^{++} \rightleftarrows Hg + Hg^{++}.$$

The reaction to the right is especially favored by the presence of an excess of iodide ions, which form the stable complex $HgI_4^=$. Upon proceeding with the titration, however, the iodide ions disappear, and the reaction is reversed, and proceeds to the left.

The reverse titration of mercurous salt with iodide gives more accurate results; inflection-potential, about +0.17 volt (against normal calomel electrode).

A very accurate titration of iodide may be carried out, according to Kolthoff and Verzijl (*loc. cit.*), by using mercuric chloride as reagent. The position of the maximum value of $\frac{\Delta E}{\Delta c}$ may be detected with an accuracy of 0.1 per cent. From the shape of the titration curve it is evident that complex ions are formed before the end-point, where all of the iodide is transformed into mercuric iodide. The stability of the complex $HgI_4^{=}$ is not large enough to give a pronounced break in potential at the point of quantitative formation of this complex.

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[43] Erich Müller and H. Aarflot, Rec. trav. chim., **43**, 874 (1924).

Even very dilute solutions can be rapidly and accurately analyzed by potentiometric titration. One hundred and twenty-five cubic centimeters of 0.0002 N KI (containing 25 parts iodide per million) could be titrated with an accuracy of 1 per cent.

125 cc. 0.0002 N KI WITH 0.001 N $HgCl_2$

| Cubic Centimeters of Reagent | $E_c$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|
| 24.03 | 0.074 | |
| 24.23 | 0.080 | 20 |
| 24.43 | 0.084 | 40 |
| 24.63 | 0.092 | 50 |
| 24.83 | 0.102 | *60 maximum* |
| 25.03 | 0.114 | 50 |
| 25.23 | 0.124 | 40 |
| 25.43 | 0.132 | |

Inflection-potential, + 0.112 volt (against normal calomel electrode), regardless of the dilution.

A titration may be finished in one minute's time by using the Müller system. The interference of chlorides is but slight; that of bromides is of more importance. In a mixture that contains equal quantities of iodide and bromide, the accuracy of the iodide titration is 0.5 per cent.

*Thiocyanate:*

$$S_{Hg_2(CNS)_2} = 1.4 \times 10^{-20}.$$

From the start of the titration, the mercurous thiocyanate decomposes into mercury and mercuric thiocyanate. This reaction has no influence on the position of the break in potential. Yet the accuracy of the determination of thiocyanate with mercury is not very great, as may be concluded from the paper of Müller and Aarflot (*loc. cit.*). The error, which is probably due to adsorption, is about 1 per cent. Better results are obtained in the reverse titration, i.e., mercurous salt with thiocyanate. Inflection potential, + 0.25 (Müller and Aarflot).

According to Kolthoff and Verzijl (*loc. cit.*), the titration of thiocyanate with mercuric perchlorate or nitrate gives very accurate results. This statement has been confirmed by R. Müller and O. Benda.[44]

*Application of the Thiocyanate Titration to the Determination of Zinc.*—Kolthoff and Verzijl (unpublished investigation) applied the thiocyanate titration to the determination of zinc. Zinc forms a slightly soluble double salt with potassium mercuric thiocyanate, $K_2Hg(CNS)_4$. A method for the determination of zinc has been based on this reaction.[45] The reagent is obtained by adding 4 moles of potassium thiocyanate to 1 mole of mercuric nitrate. A more stable solution is prepared by dissolving 14.4 g. KCNS in a little water, and dissolving 23.7 g. mercuric thiocyanate in this concentrated solution (warming a little to accelerate the speed of solution); the solution is diluted to 1 liter, and standardized against a mercuric salt solution.

*The Zinc Titration.*—An excess of the reagent is added to a measured quantity of the zinc solution, and the solution is diluted to 100 cc. The excess of the reagent is determined in an aliquot portion of the filtrate, with a mercuric salt. Sulphuric and nitric acids have no influence on the result; hydrochloric acid and chlorides interfere. According to E. Monasch,[46] ferrous, manganous, nickel, cobalt, and chromic ions have a disturbing influence on the zinc determination.

*Ferrocyanide.—Ferricyanide.*—F. Fenwick applied the bimetallic system to these determinations. She remarks:[47] " A very brief investigation was made of the possibility of titrating ferro- and ferricyanide with mercurous solution. The end-point was not particularly sharp in either case, but both titrations were possible. The ferrocyanide titration seemed the more favorable for development."

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[44] R. Müller and O. Benda, Z. anorg. Chem., **134**, 102 (1924).

[45] Cohn, Ber. **34**, 3502 (1902); de Koninck and Grandy, Chem. Zentr. **73**, II, 822 (1902); Kolthoff and van Dijk, Pharm. Weekblad, **58**, 549 (1921).

[46] E. Monasch, Pharm. Weekblad, **58**, 1652 (1921).

[47] F. Fenwick, Dissertation, Ann Arbor, Mich. (1922), p. 79.

*Cyanide.*—In the titration of cyanide with mercurous perchlorate, a quantitative decomposition of the mercurous cyanide takes place:

$$Hg_2(CN)_2 \rightarrow Hg + Hg(CN)_2.$$

The titration does not give good results, possibly because of the escape of hydrogen cyanide. The reverse titration (mercury with cyanide) is successful (Müller and Aarflot, *loc. cit.*). Inflection-potential, + 0.236 volt.

Kolthoff and Verzijl (*loc. cit.*) titrated cyanide with a mercuric salt. Although the jump in potential is greater with mercuric perchlorate or nitrate, they preferred the chloride, which does not cause any volatilization of hydrogen cyanide. The results are accurate (0.2 per cent), and the potential becomes constant very rapidly after the addition of reagent. The change in potential near the equivalence-point is presented in the following table.

TITRATION OF 25CC., APPROX. 0.1 N KCN WITH 0.1 N $HgCl_2$

| Cubic Centimeters of Reagent | $E_c$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|
| 23 | −0.202 | |
| 23.12 | −0.192 | |
| 23.18 | −0.186 | |
| 23.31 | −0.171 | |
| 23.44 | −0.145 | 370 |
| 23.51 | −0.115 | 430 |
| 23.58 | −0.00 | *1640 maximum* |
| 23.61 | 0.031 | 1030 |
| 23.64 | 0.046 | 500 |

It may be concluded from the whole titration curve that several complex ions are formed. The inflection-potential (against normal calomel electrode) is just at 0.00 volt. Hence the titration may be carried out very simply by using the Pinkhof system and titrating until the galvanometer or capillary electrometer gives no deflection, or reverses its deflection. In this way Kolthoff and Verzijl obtained accurate results in a very short time.

When both iodide and cyanide are present, only one jump in potential is obtained. It occurs after both iodide and cyanide have been transformed into mercuric salts.

*Sulphide.*—Pinkhof [48] (*vide infra*) used the mercury electrode for the determination of various metals as sulphides. He titrated mercury in a solution which contained a small excess of potassium iodide, and his results had a constant 2 per cent error which he attributed to adsorption.

Kolthoff and Verzijl (*loc. cit.*) obtained good results in the titration of sulphide with mercuric chloride when the solution contained an excess of sodium hydroxide. In this case the potential becomes constant soon after the addition of reagent; this is not the case when no hydroxide is added. The maximum is sharply defined, and the Müller system may be advantageously applied; inflection-potential, −0.200 volt (against normal calomel electrode). They found that salts had a slight effect upon the result, just as Willard and Fenwick found in the titration with silver nitrate. The effect of salts is shown in the following table:

Titration of Sulphide

| Addition | Used cc. 0.1 N Mercuric Chloride | Error, Per Cent |
|---|---|---|
| | 15.90 | −0.3 |
| 5 cc. 4 N NaOH | 15.95 | |
| 5 cc. 4 N NaOH 1 g. NaCl | 15.95 | |
| 1 g. $KNO_3$ | 15.95 | |
| 1 g. $Na_2SO_4 \cdot 10H_2O$ | 15.80 | −1.0 |
| 1 g. $Na_2S_2O_3 \cdot 5H_2O$ | 15.82 | −0.9 |
| 1 g. $Na_2SO_3 \cdot 7H_2O$ | 15.70 | −1.6 |

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[48] Pinkhof, Dissertation, Amsterdam (1919), p. 26.

Bivalent ions have the greatest influence on the result. The error is the same in a neutral medium. The titration of sulphide with mercuric chloride is advantageous in very dilute solutions. The titration with silver nitrate does not give reliable results in this case (*cf.* pp. 179–180), although the jump in potential is greater in the latter case. A 0.001 N sulphide solution (containing 16 parts of S per million) was titrated with an accuracy of 2 to 3 per cent.

*Application of the Mercury Electrode as an Indicator for Sulphide Ions.*—Pinkhof (*loc. cit.*) used 5 cc. of metallic mercury as an indicator for mercuric mercury. Mercuric ions are sent into solution and react with sulphide ions:

$$Hg^{++} + S^{=} \rightleftarrows HgS,$$

$$[Hg^{++}][S^{=}] = S_{HgS},$$

$$[Hg^{++}] = \frac{S_{HgS}}{[S^{=}]}.$$

Therefore, the mercuric-ion concentration of the solution and the potential of the electrode depend upon the sulphide-ion concentration of the solution. The electrode, therefore, behaves as a sulphide electrode.

Pure sodium sulphide for reagent purposes may be prepared according to Böttger's directions:[49] Strong alcohol (200 cc.) is added to a solution of 50 g. sodium hydroxide in 50 cc. water. After filtration through asbestos, half of the filtrate is saturated with hydrogen sulphide. The rest of the filtrate is added, and sodium sulphide is precipitated. It may be redissolved by warming to 90°, whereupon slow cooling causes the separation of prismatic crystals of the sulphide, which are collected by suction and washed with alcohol. Pinkhof recommends that the crystals be preserved under alcohol; in this way they may be kept for six months without decomposition. He found the composition to be $Na_2S \cdot 5H_2O \cdot$ Kolthoff found them to be $Na_2S \cdot 9H_2O$.

Pinkhof, using his simple system, titrated the various metals with the sulphide. Inaccurate results were obtained, probably because of adsorption. When air is excluded by means of a current of carbon dioxide, the error is decreased, but it is still appreciable. Hence, the authors can not recommend this method for accurate analyses.

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[49] Böttger, Ann. d. Chem., **223**, 335 (1884).

$As^{III}$ and $Sb^{III}$ are only precipitated in strongly acid solution (2 – 4N HCl). Inflection-potential, – 0.200 volt (against normal calomel cell). Reference electrode, Ag in 1.5 N KBr. Error in air, 10–12 per cent; in carbon dioxide, 4–5 per cent. $As^{V}$, $Sb^{V}$, and $Sn^{IV}$ require an excess of sulphide for complete precipitation, whereupon hydrogen sulphide escapes.[50] $Sn^{II}$ can not be titrated because it reduces all of the dissolved mercury ions to the metallic form. *Silver* ions are reduced by the mercury and can not be titrated. Mercuric ions are reduced to mercurous ions. This can be prevented by the addition of a small excess of potassium iodide. The titration may be performed in a bicarbonate medium with a carbon dioxide atmosphere; inflection-potential, – 0.300 volt (against normal calomel electrode). Compensation electrode, Ag in 0.01 N KI. The error is 2 per cent and increases with dilution of the mercuric solution. In 0.01 N solution it is 10 per cent. Interfering metals are removed by the addition of sodium carbonate to the solution, which contains an excess of iodide. The filtrate contains the mercuric salt.

Lead may be titrated in 0.1 N nitric acid solution. Inflection-potential, – 0.200 volt; compensation electrode, Ag in 1.5 N KBr. Error 1–2 per cent (in 0.1 N solution). In the presence of $Sn^{IV}$ and $Sb^{V}$, the solution is made alkaline after the addition of an excess of Rochelle salt, whereby the lead is transformed into a complex salt. Tartaric acid is then added until the concentration is 0.1 N, after which the lead is titrated with sulphide. The arsenic group remains in solution. Inflection-potential, – 0.280 volt; reference electrode, Ag in 0.003 N KI.

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[50] In the light of McCay's work on the sulphoxy-arseniates it is extremely unlikely that anything approaching a quantitative precipitation of the quinquivalent arsenic could be expected. *Cf.* L. W. McCay, Am. Chem. J., **10**, 459 (1888); Z. anorg. Chem., **29**, 36 (1901) J. Am. Chem. Soc., **24**, 661 (1902).

Bismuth forms an oxysulphide very readily; therefore the reagent must be added drop by drop. Bismuth sulphide has a strong adsorbing capacity; the error may be 15 per cent.

*Copper* precipitates well in sulphuric acid solution; strong adsorption; error about 10 per cent. The error is diminished by titrating in a bicarbonate medium in the presence of tartrate. Error, ± 3 per cent. Inflection-potential, $-$ 0.050 volt; compensation electrode, Ag in 0.5 N NaCl. In strongly acid solution, large amounts of halide have a disturbing action, since the mercury may reduce the copper to the cuprous state.

*Cadmium* must be titrated in tartrate solution weakly acidified with acetic or tartaric acid. Inflection-potential, $-$ 0.250 volt; comparison electrode, Ag in 0.001 N KI. Error, about 3 per cent.

*Zinc.*—The solution must not be more acid than a 0.1 N acetic acid solution. At lower acidity the titration gives good results, even in air. Inflection-potential, $-$ 0.380 volt; compensation electrode, Ag in 0.2 N KI. One of the authors (Kolthoff) added an excess of sulphide to the alkaline zinc solution and titrated back with mercuric chloride. The method was unsuccessful although various modifications were tried.

*Nickel and Cobalt.*—In bicarbonate-tartrate solution there was a regular change in the potential. Error, 10–20 per cent; inflection-potential, $-$ 0.510 volt; compensation electrode, Hg in 0.02 N KCN 0.02 N $AgNO_3$.

*Manganous* and *ferrous* ions can not be titrated with sulphide.

It is evident from the foregoing description that the titration of the metals with sulphide gives unsatisfactory results. The authors can not recommend the method. They suspect that the errors are due to inherent properties of the sulphides, and that improvement is unlikely.

When several metals are present in solution the precipitation of their sulphides does not take place as we should theoretically expect. When two metals are present together their sulphides are precipitated together, although singly they have quite different solubilities (Werner's theory should be recalled in this connection). A fractional separation of the metals by means of sulphide is not practically possible. Hence the authors omit the further details which Pinkhof gives in his dissertation.

*Thiosulphate.*—According to Kolthoff and Verzijl (*loc. cit.*), a sharp jump in potential is found in the titration of sodium thiosulphate with mercuric chloride at a point which corresponds to the complex salt $Na_2Hg(S_2O_3)_2$. The potential rapidly assumes a steady value, and the results are very accurate. The potential changes in an irregular way after the equivalence-point is reached. The titration does not give good results when sulphite is present. In neutral solution, sulphide and thiosulphate may be titrated in the presence of each other. The first jump occurs after the precipitation of the sulphide, the second after the formation of the complex thiosulphate ion.

*Hydroxyl Ions.*—*Cf.* Neutralizations, p. 227, on the titration of bases with the aid of the mercury-mercuric oxide electrode.

*Mercurous Salts.*—Mercurous salts may be titrated with chloride, bromide, iodide, or sulphocyanide. Good results are obtained. (*Cf.* titration of halides.)

*Mercuric Salts.*—Accurate results are obtained by titration with potassium iodide. Even mercuric chloride may be titrated up to great dilutions. In this case the best procedure is to add an excess of iodide, and titrate back with mercuric chloride.

**3. The Copper Electrode.**—W. D. Treadwell and L. Weiss[51] have shown in a preliminary paper that it is possible to titrate copper as cuprous thiocyanate, with a copper electrode. Their results, however, are far from accurate. According to Dutoit and von Weisse,[52] a copper electrode is unsuitable for potentiometric titrations because its potential changes in an irregular way. In agreement with Kolthoff's experience, E. Müller and A. Rudolph[53] were not successful in obtaining a jump in potential in the titration of a cupric solution, to which an excess of bisulphite was added, with thiocyanate; the titration was made at room temperature with a copper indicator electrode. They obtained a break when the titration was performed at

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[51] W. D. Treadwell and L. Weiss, Helv. Chim. Acta, **2**, 694 (1919).

[52] Dutoit and von Weisse, J. chim. phys., **9**, 578 (1911).

[53] E. Müller and A. Rudolph, Z. analyt. Chem., **63**, 102 (1923).

70° C. Error, + 0.7 per cent copper; inflection-potential, − 0.166 volt (against normal calomel electrode). The error is probably due to adsorption of the $CNS^-$ ion by the cuprous thiocyanate. The relative error increases rapidly with increasing dilution; in titrating 0.01 N copper solutions it is 7 per cent. The temperature control is of great importance; the best results are found at 70° C. At 90° the error is 15 per cent. This method can not, therefore, be recommended on the basis of the information which has been published.

*Silver and Copper.*—The silver is first titrated with thiocyanate, with a silver indicator electrode. After reaching the inflection-potential (0.21 volt), the liquid is filtered, and the filtrate is titrated at 70° after adding bisulphite, with a copper electrode as indicator. The reagent is added slowly to permit the potential to reach a steady value. Inflection-potential, − 0.166 volt (against normal calomel electrode). The filtration of the silver thiocyanate is necessary because it would otherwise be reduced by the bisulphite to form metallic silver, thus causing erroneous results since a silver electrode gives erratic values in the titration of cuprous ion with thiocyanate.

**4. The Iodine Electrode.**[54]—*General Remarks.*—The potential of the iodine electrode is represented by the equation:

$$E = \varepsilon_0 + \frac{0.059}{2} \log \frac{[I_2]}{[I^-]^2} \quad (25°).$$

As is well known, iodine is slightly soluble, and it is therefore advantageous in many instances to use the saturated iodine electrode, whereupon the iodine concentration $[I_2]$ is constant and equal to the solubility (0.00134 molar at 25°). We then have:

$$E = \varepsilon_0' - 0.059 \log [I^-] = \varepsilon_0' + 0.059 p_I.$$

where $\varepsilon_0'$ is 0.541 volt against the normal hydrogen electrode.

In a solution that contains iodide ion and iodine, reaction between the two is possible in the sense of the equation:

$$I_2 + I^- \rightleftarrows I_3^-,$$

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[54] I. M. Kolthoff, Rec. trav. chim., **41**, 172 (1922).

and, according to the law of mass action:

$$\frac{[I_2][I^-]}{[I_3^-]} = K.$$

At 18°, K is equal to $15 \times 10^{-3}$ (Dawson).[55]

Since the solubility of iodine is $1.09 \times 10^{-3}$ at 18°, we have:

$$\frac{[I^-]}{[I_3^-]} = \frac{1.15 \times 10^{-3}}{1.09 \times 10^{-3}} = \text{about 1 (in a saturated iodine solution).}$$

Hence, half of the total iodide is transformed into complex $I_3^-$ ions; and if the total concentration is equal to $I^-$, we have:

$$E = \varepsilon_0' - 0.059 \log \tfrac{1}{2}[I^-],$$

or

$$E = \varepsilon_0' + 0.017 - 0.059 \log [I^-].$$

From this we see that the potential of the iodine electrode depends upon the iodide concentration in the same way as that of a metal electrode depends upon the concentration of univalent metal ions (opposite sign in change of potential term). The iodine electrode has the following special characteristic: Iodine reacts with water, as represented by the equation:

$$3I_2 + 3H_2O \rightleftarrows 6H^+ + IO_3^- + 5I^-$$

with the equilibrium constant of $2.45 \times 10^{-47}$ at 25° C. (Sammet).[56]

From this value we see that there is almost no reaction between the free iodine and water. If, however, we add a substance that reacts with iodide ion, the reaction may proceed to the right. This is the case, for example, in the titration of iodide with silver nitrate, with the iodine electrode. When the equivalence-point has been reached, an excess of silver nitrate reacts with iodine with the formation of iodate and silver iodide. The equilibrium conditions are dependent upon the solubility product of the silver iodide. The less soluble the iodide, the more nearly the reaction proceeds to completion toward the right. If the iodide is slightly dissociated the considerations are similar to those met in the case of mercuric iodide.

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[55] Dawson, J. Chem. Soc., **85**, 467 (1904).

[56] Sammet, Z. Elektrochem., **11**, 293 (1905); Z. physik., Chem., **53**, 641 (1905).

When iodate is formed after the equivalence-point has been reached, we are dealing with the iodate electrode, whose potential, according to Sammet (*loc. cit.*) is represented by:

$$E = \varepsilon_0 + \frac{0.0591}{10} \log \frac{[H^+]^{12}[IO_3^-]^2}{[I_2]}.$$

In a normal solution of iodic acid which is saturated with respect to iodine, $\varepsilon_0$ is equal to 1.158 volt (referred to N $H_2$ electrode). From the equation we see that the potential is dependent, to a very high degree, upon the hydrogen-ion concentration. The larger the latter, the more positive will be the potential. For this reason, the jump in potential in the titration of iodide with silver nitrate or mercuric salt depends, to a great extent, upon the hydrogen-ion concentration; in acid solution it is much larger than in a neutral medium. When the iodide which is formed is much more soluble than silver iodide, as is the case with lead or thallous iodide, enough iodide ions remain in solution, after the equivalence-point has been reached, to prevent the iodate formation. It is even possible to transform lead iodide quantitatively to free iodine with the aid of iodate. Therefore, when we are titrating an iodide solution with thallous salt, using the iodine electrode as indicator electrode, the iodide concentration changes at all points of the titration curve according to:

$$[I^-] = \frac{S_{TlI}}{[Tl^+]},$$

whereas the iodide is not transformed into iodate.

In the titration of a single substance, the iodate formation has no influence on the result of the titration. If, however, we have two substances together, for example, iodide and bromide, which we are titrating with silver nitrate, a small error may result from iodate formation. After the precipitation of the iodide, most of the reagent is used for the precipitation of the bromide, whereas a small quantity reacts with iodine to form iodate.

From the above, it is evident that the iodine electrode may be used in all cases where a slightly dissociated or complex iodide is formed. Its application may be of distinct advantage in the titration of mercuric salts, since the mercury electrode is not reversible to mercury ions.

*Electrode.*—A piece of bright platinum, or better, platinum gauze, in contact with iodine, serves well as an electrode. The best way to saturate the liquid with iodine is to add a little of a freshly prepared alcoholic iodine solution. Its quantity is of no significance; 2 to 10 drops of a 10 per cent tincture to 100 cc. of liquid will do. The authors desire to lay stress on the fact that the alcoholic solution should be freshly prepared, since it decomposes on standing, to form a little iodide. This might cause an error, especially in the titration of dilute solutions.

*Determination of Iodide with Silver Nitrate.*[57]—In the titration of a neutral iodide solution, the jump in potential occurs 0.8 per cent too early, probably because of the adsorbing properties of silver iodide. The result is improved by titration in the presence of sulphuric acid, the error being only 0.2 per cent. The jump in potential is much greater than in neutral solution, as stated above. When titration is carried out in acid solution, the silver iodide flocculates from the start of the titration, whereas in a neutral medium the iodide remains in colloidal solution and flocculates just before the equivalence-point is reached. Owing to the high degree of dispersion, the adsorbing capacity of the iodide is much greater in the latter case than in an acid medium. After the end-point is reached, the silver nitrate reacts with the iodine to form iodate, and the brown color of the liquid disappears. The titration may be performed with very dilute solution; a 0.001 N $I^-$ solution may be determined with an accuracy of about 1 per cent.

In the presence of bromide or chloride, the jump in potential at the equivalence-point is less pronounced. In harmony with the results of Liebich with the silver electrode (*cf.* p. 169), Kolthoff found that the error due to the adsorption by silver iodide is descreased in the presence of bromide. In the titration of a mixture of quivalent amounts of iodide and bromide, the jump in potential was found 0.2 per cent too late (in iodide solution alone, 0.8 per cent too soon). In the presence of bromide, the silver iodide does not flocculate at the first equivalence-point.

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[57] I. M. Kolthoff, Rec. trav. chim., **41**, 176 (1922).

When the iodide is titrated in the presence of hydrochloric acid, the same results are obtained as when sulphuric acid is used, although the jump in potential is smaller in the former case. Yet it is possible to titrate iodide in the presence of 100 times the amount of chloride, with an accuracy of 0.5 per cent.

The titration of bromide or chloride with silver nitrate, with the iodine electrode, does not give accurate results.

*Titration of Iodide with Mercuric Salts.*—In general, mercuric nitrate dissolved in dilute nitric acid can not be recommended as a reagent, because it oxidzes the iodide. The error may be rather large, 1.5 to 5 per cent, especially in strong iodide solution (0.1 N); in very dilute solution the error is less pronounced. In principle, it is better to use mercuric perchlorate, a solution of which may be readily prepared (*cf.* p. 186). The titration curve has a peculiar shape, due to complex formation (*cf.* Kolthoff, *loc. cit.*); no distinct break in potential occurs at the point where the reaction:

$$Hg^{++} + 4I^- \rightleftarrows HgI_4^=$$

is complete. The complex constant is too large for strong variations in ion concentrations to be found. A sharp break is found, however, at the point where mercuric iodide is quantitatively formed. The titration gives very accurate results, even in dilute solution. Inflection-potential, + 0.580 volt (against normal calomel electrode). Some results are given in the following table:

| Solution to be Titrated | Cubic Centimeters $Hg(ClO_4)_2$ Used | Normality | Error in Per Cent |
|---|---|---|---|
| 100 cc. 0.025 N KI | 25.02 cc. | 0.1 N | +0.1 |
| 100 cc. 0.0025 N KI | 24.92 cc. | 0.01 N | −0.3 |
| 100 cc. 0.00025 N KI | 25 cc. | 0.001 N | |
| 100 cc. 0.0001 N KI | 10.02 cc. | 0.001 N | +0.2 |
| 100 cc. 0.00005 N KI | 5 cc. | 0.001 N | |

Hence, a solution containing as little as 6 parts iodide per million may be titrated with an accuracy of at least 0.5 per cent.

In the presence of bromide, the jump in potential is not very large and the accuracy of the titration is much smaller than with iodide alone. A mixture of equivalent amounts of iodide and bromide may be titrated with an accuracy of 0.5 per cent. The disturbing action of chloride is much less than that of bromide. When the ratio of $I^-$ to $Cl^-$ is 1 : 20, very accurate results are still obtained. In this case we may use mercuric chloride for a reagent, as well as mercuric perchlorate.

Bromides and chlorides may also be titrated with mercuric perchlorate, with the iodine electrode. The jumps in potential at the equivalence-point are much smaller than in the case of the iodide, but good results are still obtained. It is also possible to determine the iodide, bromide, and chloride separately in a mixture of the three halides. The accuracy is not very high, however. As we have seen, iodide may be titrated in the presence of the same amount of bromide, with an accuracy of 0.5 per cent. But the potential break after the bromide is transformed into mercuric bromide is still less pronounced when chloride is present. The accuracy in this case is not larger than 1 to 2 per cent. In order to show how the potential changes, the authors give, in the table on page 202, the titration of a mixture of 10 cc. of 0.1 N KI, 10 cc. 0.1 N KBr, and 10 cc. of 0.1 N KCl with approximately 0.1 N $Hg(ClO_4)_2$. The titration curve is given in Fig. 40.

*Titration of Mercuric Mercury.*—The iodine electrode is especially convenient for the titration of mercury in mercuric chloride. The sublimate can be titrated directly with a standardized iodide solution. The inflection-potential is 0.550 volt (against normal calomel electrode). The results of the titration are accurate.

*Titration of Thallous Salts.*—Because of the fact that thallous iodide is slightly soluble, we may make use of the titration of thallous salts with iodide. The solubility product of thallous iodide is rather large (about $10^{-8}$); therefore, only solutions that are 0.05 N or stronger give a distinct jump in potential at

| Cubic Centimeters of Reagent Added | $E_c$ | $\frac{\Delta E}{\Delta c}$ |
|---|---|---|
| 0 | 0.308 | |
| 5 | 0.384 | |
| 9 | 0.426 | |
| 9.5 | 0.446 | |
| 10 | 0.476 | 60 |
| 10.1 | 0.496 | *200* First maximum |
| 10.2 | 0.512 | 160 |
| 10.3 | 0.526 | 140 |
| 10.4 | 0.536 | 100 |
| 11 | 0.558 | 36 |
| 15 | 0.618 | |
| 19 | 0.682 | |
| 19.5 | 0.684 | |
| 20 | 0.690 | |
| 20.2 | 0.692 | 10 |
| 20.3 | 0.693 | 10 |
| 20.4 | 0.696 | *30* Second maximum |
| 20.5 | 0.697 | 10 |
| 20.7 | 0.698 | 10 |
| 21 | 0.700 | 7 |
| 23 | 0.718 | |
| 25 | 0.738 | |
| 27 | 0.756 | |
| 29 | 0.780 | |
| 29.5 | 0.792 | |
| 30 | 0.812 | |
| 30.2 | 0.824 | 60 |
| 30.4 | 0.838 | *70* |
| 30.5 | 0.846 | *80* Third maximum |
| 30.6 | 0.852 | 60 |
| 30.7 | 0.856 | 40 |
| 31 | 0.872 | 50 |
| 32 | 0.894 | 22 |
| 33 | 0.906 | |

First maximum: 10.1 cc. (calculated for iodide 10.08 cc.)
Second maximum: 20.4 cc. bromide (20.4 − 10.1) = 10.3 cc. (calculated for bromide 10.35).
Third maximum: 30.5 cc. chloride (30.5 − 20.4) = 10.1 (calculated for chloride 10.15).

the equivalence-point. The accuracy is about 0.2 per cent; inflection-potential, 0.456 volt (against normal calomel electrode).

*Lead* and *bismuth* iodides are too soluble to give good end-points in the titration. A good maximum occurs only in the titration of 1 N lead salts; more dilute solutions can not be titrated. Bismuth salts give a small jump in potential when titrated in nitric acid solution; in the presence of hydrochloric acid, no jump at all in potential occurs. Therefore, the iodine electrode can not be recommended for the titration of lead or bismuth salts.

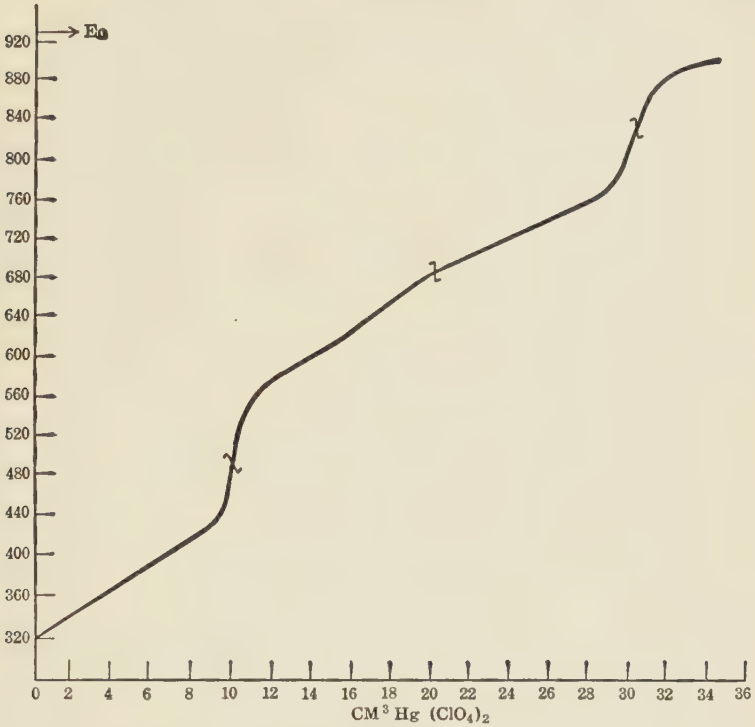

FIG. 40.—Titration of a mixture of halides with mercuric perchlorate, using the iodine electrode.

## CHAPTER X

## NEUTRALIZATIONS

In Part I a full account was given of the theory of neutralizations, the shape of the neutralization curve, and the magnitude of the change in potential at the equivalence-point. Therefore, the reader is referred to Part I for the theory of these reactions, and will find in the present chapter the practical details and applications of the electrodes which are used in quantitative neutralizations.

**1. The Hydrogen Electrode.**—

$$p_H = \frac{-E_H}{0.0591} \text{ (25° C.) (against normal hydrogen electrode).}$$

The reader is referred to W. M. Clark, " The Determination of Hydrogen Ions," for details about different forms of hydrogen electrodes. A very convenient and suitable electrode has been described by J. H. Hildebrand [1] in his classical paper " Some Applications of the Hydrogen Electrode in Analysis, Research, and Teaching."

The electrode consists of a platinum foil welded to a short piece of platinum wire, which is sealed through the end of a glass tube where it makes contact with a copper wire, either by means of a soldered joint or a mercury globule. The glass tube is within a slightly wider tube which contains a side arm near the top for the admission of hydrogen gas, and a bell-shaped enlargement at the bottom to protect the foil and confine the hydrogen, which must bathe its upper half. A wide notch is cut in the bottom of the bell to allow the liquid to rise high enough to cover the lower half of the foil. After the inner tube has been adjusted to the proper height, it is fastened to the outer tube by means of marine glue. Before this is done, however, the platinum foil is bent into an S shape, and is platinized by the usual process. One of the authors (Kolthoff) always uses a small piece of platinized platinum wire ending in a sharp point. With an electrode of this kind the reading becomes constant sooner. The delay is only appreciable at the start, and again at the end-point where the jump occurs. It is more convenient to make two round holes for the escape of hydrogen, instead of the notch in the glass of the bell-shaped part.

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[1] J. Am. Chem. Soc., **35**, 847 (1913).

W. D. Treadwell and L. Weiss[2] have described a very inexpensive form of electrode, which contains about 25 cents' worth of noble metal, and which quickly gives reproducible potential values: The outside of a strong 6-mm. tube of unglazed porcelain is coated with a thin layer of gold by soaking the tube in gold chloride solution, followed by gentle heating over a flame. The layer is then fortified by electrolytic deposition of gold from a cyanide bath. The current density must be so carefully regulated that a well-adhering deposit with a coarse surface is produced. The lower portion of the tube, thus gilded to about 7 cm. of its height, is then given an extemely thin (*hauchdünne*) electrolytic plate of palladium black.

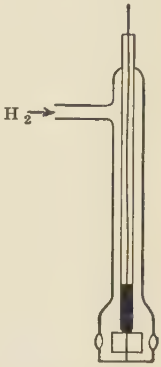

FIG. 41.—Dip electrode.

Two of these electrodes are used as a cell for titration purposes (Treadwell system). One of them contains a buffer solution of the $p_H$ value that is expected at the end-point. Hydrogen is passed through at a rate of 2 or 3 bubbles per second. In his simple system, J. Pinkhof[3] uses cadmium amalgam in contact with various solutions, instead of a hydrogen electrode, as a reference electrode. These electrodes are readily reproducible and are electromotively equivalent to hydrogen electrodes which dip into various solutions of known hydrogen-ion concentrations. The electrodes that Pinkhof used were provided with 11–13 per cent cadmium amalgam.

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[2] W. D. Treadwell and L. Weiss, Helv. Chim. Acta, **3**, 433 (1920).

[3] J. Pinkhof, Chem. Weekblad, **16**, 1168 (1919).

REFERENCE ELECTRODES OF PINKHOF

| Composition of Electrode Solution | | Potenial Against 0.1 N Calomel Electrode | Equivalent to a Hydrogen Electrode in a Solution of [H$^+$] |
|---|---|---|---|
| Cd(NO$_3$)$_2$ | 1.3 N | −0.696 | $10^{-6}$ |
| CdCl$_2$ | 0.1 N | −0.754 | $10^{-7}$ |
| CdI$_2$<br>KI | 0.1 N<br>0.21 N | −0.812 | $10^{-8}$ |
| CdI$_2$<br>KI | 0.1 N<br>0.6 N | −0.870 | $10^{-9}$ |
| CdI$_2$<br>KI | 0.1 N<br>1.05 N | −0.929 | $10^{-10}$ |

P. F. Sharp and F. H. MacDougall,[4] who have simplified the preparation of the electrodes, give the following list:

REFERENCE ELECTRODES OF SHARP AND MACDOUGALL

| Electrode Solutions. Dilute the Quantities Given to a Total Vol. of 100 cc. | | | Potential Against N Calomel Electrode | Equivalent to a H$_2$ Electrode in Solution of [H$^+$] |
|---|---|---|---|---|
| | | | 12–12.5 Per Cent Lead Amalgam and Lead Iodide | |
| cc. | N | Salt | | |
| 0.52 | 2 | KI | −0.5195 | $10^{-4}$ |
| 2.90 | 2 | KI | −0.5609 | $10^{-4.7}$ |
| 6.14 | 2 | KI | −0.5786 | $10^{-5}$ |
| 67.50 | 2 | KI | −0.6378 | $10^{-6}$ |
| | | | 12–12.5 Per Cent Cadmium Amalgam | |
| 10<br>0.20 | 0.5<br>2.0 | CdSO$_4$<br>KI | −0.6967 | $10^{-7}$ |
| 10<br>10.14 | 0.5<br>2 | CdSO$_4$<br>KI | −0.7560 | $10^{-8}$ |
| 10<br>26.40 | 0.5<br>2 | CdSO$_4$<br>KI | −0.8150 | $10^{-9}$ |
| 12.00<br>48.70 | 0.5<br>2 | CdSO$_4$<br>KI | −0.8742 | $10^{-10}$ |

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[4] P. F. Sharp and F. H. MacDougall, J. Am. Chem. Soc., **44**, 1193 (1922); *cf.* also H. T. Beans and E. Little, J. Ind. Eng. Chem., **17**, 413 (1925).

A. B. Hastings [5] has described a convenient hydrogen electrode vessel which is adapted for titrations.

The authors recommend the electrode of J. Hudig and W. Sturm [6] for the determination of the acidity and titration curve of soils.

Hydrogen electrode vessels for use with tannery liquors have been described by J. A. Wilson and E. J. Kern.[7]

*Hydrogen Generators.*—Hydrogen generated from sulphuric acid with pure zinc is usually used. Care should be taken to displace all oxygen from the generator and to free the hydrogen from impurities, especially arsenic. For this purpose the authors always wash the gas by passing it through silver nitrate, potassium permangante, and water.

Compressed hydrogen of high purity is now on the market. It is satisfactory for hydrogen electrode work; Fales and Vosburgh [8] pass it through alkaline permanganate, alkaline pyrogallol, water, and cotton wool. Cullen [9] passes the tank hydrogen through solutions of mercuric chloride, permanganate, pryogallol, dilute sulphuric acid, and water. The compressed hydrogen is especially valuable for the immersion electrode which the authors use in quantitative titrations, where an abundant supply of hydrogen is required.

Electrolytic generators have been employed very frequently; they are especially satisfactory when a moderate supply of hydrogen of highest purity is required at frequent intervals, or steadily, over long periods of time. (*Cf.* Clark, " The Determination of Hydrogen Ions.")

*Disturbing Factors in the Use of the Hydrogen Electrode.*—Oxygen gives the electrode a positive charge and is very dangerous. In order to avoid the presence of oxygen, titrations should be carried out in vessels closed by means of rubber or wooden stoppers with the requisite holes for inlet and outlet of hydrogen, contact with the calomel electrode, etc. The presence of air is made evident by the inconstancy of the potential.

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[5] A. B. Hastings, J. Biol. Chem., **46**, 463 (1921).

[6] J. Hudig and W. Sturm, Chem. Weekblad, **16**, 473 (1919).

[7] J. A. Wilson and E. J. Kern, J. Ind. Eng. Chem., **17**, 74 (1925).

[8] H. A. Fales and W. C. Vosburgh, J. Am. Chem. Soc., **40**, 1291 (1918).

[9] G. E. Cullen, J. Biol. Chem., **30**, 369 (1917).

Impurities in the hydrogen, such as hydrogen sulphide, hydrocarbons, etc., may poison the electrode; therefore, the purification mentioned above is necessary.

Oxidizing agents are reduced in the hydrogen electrode; we can not, therefore, make measurements in the presence of these substances (such as ferric iron, bichromate, nitric acid, etc.). Nor can the hydrogen electrode be used in the presence of reductants, as they make the potential much too negative (e.g., sulphurous acid). In some instances where the potential of the reductant is not reproducible, it has no disturbing action (hydrazine).

Organic substances that can be reduced also interfere. The platinum black of the electrode catalyzes the reduction. Aromatic compounds, in particular, may have a disturbing action; even aniline and phenol may interfere under special conditions. Many alkaloids and dyestuffs can not be examined with the hydrogen electrode.

Metals that stand below hydrogen in the electromotive force series, and also lead, are reduced on the electrode; therefore they have an interfering action.

Fortunately, we have other electrodes for the measurement of hydrogen-ion concentrations, as we shall see in the following sections.

*Applications of the Hydrogen Electrode.*[10]—W. Böttger [11] was the first to apply the hydrogen electrode for titration purposes. He determined the neutralization curves of hydrochloric, sulphuric, acetic, proprionic, isobutyric, lactic, tartaric, mellitic, citric, succinic, phosphoric, arsenic, arsenous, boric, and carbonic acids; also those of sodium hydroxide, benzylamine, aniline, and ammonia. He did not get very reliable results with the last three substances as they affected the electrode. He also made a study of the titration of a weak acid in the presence of a strong one (acetic acid in the presence of hydrochloric acid), and of a weak base in the presence of a strong one (benzylamine in the presence of sodium hydroxide). We see from this that Böttger, as early as 1897, had made a complete study of the application of the hydrogen electrode to neutralizations.

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[10] *Cf.* Furman, Chapter XIII, p. 829, Taylor's "Physical Chemistry," D. Van Nostrand Co., for a review of other applications.

[11] W. Böttger, Z. physik. Chem., **24**, 253 (1899); Die Anwendung der Elektrometers als Indikator beim Titrieren von Säuren und Basen. Dissertation, Leipzig (1897), 53 pp.

Later publications have not brought a very different point of view. Nevertheless, the paper of J. H. Hildebrand [12] is of great importance, as he simplified the apparatus (immersion electrode, use of voltmeter, etc.) and laid stress upon the practical and theoretical significance of the use of the hydrogen electrode. Hildebrand also determined various neutralization curves (and displacement curves, i.e., curves obtained in the titration of salts of weak acids with a strong acid, or salts of weak bases with a strong base). He gave the neutralization curve of citric acid with ammonia, also those of oxalic, maleic, and fumaric acids, magnesium ammonium phosphate, ferrous sulphate, beryllium sulphate, aluminum sulphate, and salts of rare earths. Hildebrand and Harned [13] made a practical application of these titrations to the determination of magnesium as magnesium hydroxide in the presence of calcium (analysis of dolomite).

The method does not give quite accurate results, however; we may conclude from the results of Harned that the method may be as much as 5 per cent in error. I. M. Kolthoff [14] confirmed these results, and therefore can not recommend the method for general use. The potential reaches constancy very slowly; improvement is made by adding an excess of alkali and titrating back with standard acid. In agreement with Pinkhof (Diss. Amsterdam, 1919), Kolthoff found that the accuracy in the titration of magnesium chloride was about 1 per cent. In the titration of magnesium sulphate the deviation was much higher, 5 per cent or more, owing to the formation of basic salts. He obtained better results by titrating at a temperature of 70°, under which conditions the accuracy is about 1 per cent, when the concentration of the magnesium is more than 0.5 N. Moreover, the potential becomes constant very soon after the addition of reagent. If the concentration of the magnesium is less than 0.5 N, the jump in potential at the end-point is so small that reliable results can not be obtained. For the reasons given the authors can not recommend this titration of magnesium for general use.

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[12] J. H. Hildebrand, J. Am. Chem. Soc., **35**, 847 (1913).

[13] See Hildebrand (*loc. cit.*), p. 869; see also Hildebrand and Harned, 8th Internat. Cong. Applied Chem., **1**, 217 (1912).

[14] I. M. Kolthoff, Rec. trav. chim., **41**, 787 (1922).

Pinkhof [15] used the hydrogen electrode for the titration of acetates with hydrochloric acid. Good results were obtained only when the concentration was greater than 1 N. (The same is true with indicators.[16]) Pinkhof titrated ammonium salts by adding an excess of sodium hydroxide and titrating back with acid. Here again, good results are obtained only in the titration of concentrated solutions.[17] Pyrophosphate may be tirated to secondary phosphate with acid. Pinkhof did not succeed in the titration of alkaloids, probably because of their reduction at the hydrogen electrode. Fr. Müller [18] and Kolthoff encountered the same difficulty; yet J. C. Krantz [19] was able to titrate some alkaloids, using the hydrogen electrode.

Pinkhof also determined strong acids in the presence of acetic acid. It may be concluded from theoretical considerations, and from the work of Treadwell and Weiss [20], that this application is very limited. Thus, it is not possible to determine hydrochloric acid in the presence of formic acid by this method. In general, it may be said that in colorless solutions we can not do more with the hydrogen electrode than with indicators.[17]

G. L. Wendt and A. H. Clarke [21] determined the neutralization curve of phosphoric acid by calcium hydroxide. They did not observe a jump in potential at the point corresponding to the formation of secondary phosphate.

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[15] Pinkhof, Dissertation, Amsterdam (1919), p. 44.

[16] *Cf.* I. M. Kolthoff, The Use of Indicators.

[17] *Cf.* I. M. Kolthoff, The Use of Indicators.

[18] Fr. Müller, Z. Elektrochem., **30**, 587 (1924).

[19] J. C. Krantz, J. Am. Pharm. Assoc., **14**, 294 (1925).

[20] W. D. Treadwell and L. Weiss, Helv. Chim. Acta, **3**, 433 (1920).

[21] G. L. Wendt and A. H. Clarke, J. Am. Chem. Soc., **45**, 881 (1923).

The titration of boric acid, especially in the presence of polyhydroxy organic compounds, has been determined by a number of investigators. Attention is called especially to the work of J. van Liempt [22] and of M. G. Mellon and V. N. Morris.[23]

E. C. Gilbert [24] titrates hydrazine and its salts, using the hydrogen electrode. He found a jump in potential at the point corresponding to the mono-salt (basic salt).

The hydrogen electrode has been shown to be of great value in many practical and industrial processes. It is suitable for use in the titration of fruit juices and beverages (beer, milk, etc.); testing and purification of water for household and industrial uses: testing of soil extracts, sludges, tannery liquids, soaps, etc.

R. B. Smith and P. M. Giesy [25] determined the alkalinity of magma magnesiae with the hydrogen electrode.

E. A. Keeler [26] has described a number of applications to industrial processes, together with automatic instruments of the kind used in recording pyrometers. The recording instrument may be be applied, by means of appropriate electrical connections, to the mechanical addition of reagents, the releasing of alarm signals at predetermined $p_H$ values of solutions, etc. (*Cf.* Chapter VIII, § 5.) Keeler has also described equipment for the testing of boiler water, the carbonation of cane sugar juice, the preparation of casein from milk, the investigation of soaps, etc.

R. Kremann and F. Schöpfer [27] have applied the hydrogen electrode to the determination of the acid number of fatty acids and of fats, although the air electrode is more suitable for this purpose (*cf.* § 2 following).

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[22] J. van Liempt, Rec. trav. chim., **39**, 358 (1920); Z. anorg. Chem., **111**, 151 (1920).

[23] M. G. Mellon and V. N. Morris, J. Ind. Eng. Chem., **16**, 123 (1924); **17**, 145 (1925); Proc. Indiana Acad. Sci., **33**, 85 (1924).

[24] E. C. Gilbert, J. Am. Chem. Soc., **46**, 2648 (1924).

[25] R. B. Smith and P. M. Giesy, J. Am. Pharm. Assoc., **12**, 955 (1923); **13**, 1118, 1119 (1924).

[26] E. A. Keeler, J. Ind. Eng. Chem., **14**, 395 (1922); Power, **55**, 126, 768 (1922).

[27] R. Kremann and F. Schöpfer, Die Seife, **8**, No. 35 (1922).

On titrations in ethyl alcohol as a solvent, see E. R. Bishop, E. B. Kittredge, and J. H. Hildebrand.[28]

**2. The Oxygen and Air Electrodes.**—*General Discussion.*—When oxygen is supplied to an "unattackable electrode," e.g., one of platinized platinum, there is a tendency to form oxygen ions, and the electrode becomes positively charged:

$$\tfrac{1}{2}O_2 + 2e \rightleftarrows O^=.$$

This tendency is proportional to the partial pressure (concentration) of the gas. At constant temperature:

$$\frac{[O^=]}{\tfrac{1}{2}[O_2]} = K.$$

Furthermore, we have:

$$[H^+][OH^-] = K_w,$$

and

$$\frac{[O^=][H^+]}{[OH^-]} = K',$$

or

$$[O^=] = \frac{[OH^-]}{[H^+]}K'.$$

Upon combining these equations, we have:

$$[O^=] = \frac{K_wK'}{[H^+]^2}.$$

According to the Nernst equation, the potential of the oxygen electrode is given by:

$$E = \frac{0.059}{2}\log\frac{P}{[O^=]} = c + \frac{0.059}{2}\log\frac{[H^+]^2}{K_wK'},$$

or

$$E = \varepsilon_0 + 0.059 \log [H^+] \quad (\text{at } 25^\circ).$$

It is therefore obvious that the oxygen electrode acts as an indicator for hydrogen ions.

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[28] E. R. Bishop, E. B. Kittredge and J. H. Hildebrand, J. Am. Chem. Soc., **44**, 135 (1922).

It has been shown conclusively in a number of investigations [29] that the potential of the oxygen electrode is irreversible, the probable explanation being that oxide formation enters as a complicating factor. Although the oxygen electrode never reaches a steady potential value, the magnitude of the variation is only of the order of 5–10 millivolts per hour in acid solution after approximate saturation of the electrode with the gas. In alkaline solution the drift is about six times as great. N. H. Furman [30] found that an electrode that was saturated with oxygen or air could be used in ordinary analytical determinations in spite of this variation. The change in the electromotive force does not mask the trend of the titration curve, which may be constructed in a few minutes. Usually about fifteen to twenty minutes' passage of the gas serves to saturate the electrode before the titration is commenced.

Theoretically, we should expect that the air electrode would be 0.008 volt less positive than the oxygen electrode under similar conditions. Smale [31] found that the difference was ten to fifteen times as great.

The oxygen and air electrodes that Furman used were of the Hildebrand type. The electrodes were supplied either from a cylinder of oxygen, or with gas generated electrolytically in 10 per cent sodium hydroxide solution at a nickel anode. The gas was washed by acidified permanganate solution, and by concentrated sodium hydroxide. The permanganate washing was omitted when air was used instead of pure oxygen.

P. A. van der Meulen and F. Wilcoxon [32] prefer a bright platinum electrode, which gives fairly constant potential values. The platinum acts as an oxygen electrode in a more or less completely saturated condition, depending on the preliminary treatment. Furman (*loc. cit.*) found that the air electrode was much less influenced by minor changes in manipulation than the simple platinized or bright platinum electrodes. A less sensitive potentiometer may be used with the air electrode.

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[29] *Cf.* Crotogino, Z. anorg. Chem., **24**, 258 (1900); Bose, Z. physik. Chem., **34**, 730 (1910); Wilsmore, *ibid.*, **35**, 291 (1900); Czepinski, Z. anorg. Chem., **30**, 1 (1902); Westhaver, Z. physik. Chem., **51**, 83 (1905); Lewis, J. Am. Chem. Soc., **28**, 158 (1906); Schoch, J. Phys. Chem., **14**, 665 (1910); Foerster, Z. physik. Chem., **69**, 336 (1910).

[30] N. H. Furman, J. Am. Chem. Soc., **44**, 2685 (1922).

[31] Smale, Z. physik. Chem., **14**, 600 (1894); see also Hoeper, Z. anorg. Chem., **20**, 423 (1899).

[32] P. A. van der Meulen and F. Wilcoxon, Ind. Eng. Chem., **15**, 62 (1923).

Satisfactory titration curves are found either in the presence or absence of oxidizing agents. In the absence of pronounced oxidizing and reducing agents, a fair approximation of the hydrogen-ion concentration may be made after empirical calibration of the E.M.F. values of the oxygen (or air) electrode against a normal calomel cell, with standard buffer mixtures.[33]

H. P. Barendrecht [34] made use of the oxygen electrode for $p_H$ determinations in connection with enzyme studies. A. K. Goard and E. K. Rideal [35] employed a carefully controlled oxygen electrode in the measurement of certain otherwise inaccessible potentials.

The air electrode is very convenient, according to Furman [36] for the determination of free acid in bichromate, or free alkali in chromate, or in the analysis of mixtures of chromate and bichromate. He also used it in the determination of various acids, e.g., hydrochloric, nitric, perchloric, acetic, etc.

G. S. Tilley and O. C. Ralston [37] used the air electrode to detect the point where metals are completely removed from solution by hydrolytic action. They thus controlled the oxidation of ferrous iron by manganese dioxide or by aeration. This is of importance in the purification of copper sulphate solutions, with calcium carbonate and air, before recovery of the copper. The electrode is ineffective when the oxidation is slow.

R. Kremann and F. Schöpfer [38] used the bright platinum oxygen electrode or air electrode for the determination of the acid number of acids and fats. They recommend the use of 0.1 N alcoholic potassium hydroxide. If the soap is deposited on the electrode the latter may be cleaned by scraping. The jump in potential generally occurs at the point where phenolphthalein changes color.

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[33] *Cf.* G. H. Montillon and N. S. Cassel, Trans. Am. Electrochem. Soc., **45**, 259 (1924); see also H. T. S. Britton, J. Chem. Soc., **125**, 1572 (1924).

[34] H. P. Barendrecht, Proc. K. Akad. Wetensch. (Amsterdam), **22**, 126 (1919).

[35] A. K. Goard and E. K. Rideal, Trans. Faraday Soc., **19**, 740 (1924).

[36] N. H. Furman, Trans. Am. Electrochem. Soc., **43**, 79 (1923).

[37] G. S. Tilley and O. C. Ralston, Trans. Am. Electrochem. Soc., **44**, 31 (1923).

[38] R. Kremann and F. Schöpfer, Die Seife, **8**, No. 35 (1922).

S. Popoff and M. J. McHenry [39] used the bare platinum electrode (*cf.* van der Meulen and Wilcoxon) for the titration of alkaloids. The electrode is cleaned, after every titration, by immersion in cleaning mixture (dichromate-sulphuric acid), followed by thorough washing. Curves are given for the titration of quinine, quinine sulphate, cocaine, cocaine hydrochloride, cinchonidine, and strychnine.

R. B. Smith and P. M. Giesy [40] studied the titration of ferric chloride with sodium hydroxide with the aid of the oxygen electrode.

Arthur and Keeler [41] have described a continuous recording apparatus for the measure and control of the alkalinity of boiler feed water, by means of the air electrode − 0.1 N calomel electrode cell. The electromotive-force readings were calibrated empirically in terms of grains of alkalinity per gallon of water.

In a brief note, H. H. Willard and F. Fenwick [42] have described the application of the bimetallic system to quantitative neutralizations. Their usual polarized system (*cf.* Chapter VIII, § 4) was used. When the solution to be titrated contained a small concentration of hydrochloric acid, the action of the galvanometer was extremely sluggish in the region of the neutral point.

" An apparently enormous resistance was set up within the solution; the measuring instruments lost their sensitivity and no end-point was obtainable. The addition of potassium bromate did not improve matters. When, however, a neutral solution of hydrogen peroxide (neutralized with bromphenol blue as indicator) was added, the normal sensitivity continued throughout; a potential difference persisted to within 0.3 to

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[39] S. Popoff and M. J. McHenry, J. Am. Pharm. Assoc., **14**, 473 (1925).

[40] R. B. Smith and P. M. Giesy, J. Am. Pharm. Assoc., **12**, 855 (1922).

[41] Arthur and Keeler, Power, **55**, 768 (1922).

[42] H. H. Willard and F. Fenwick, J. Am. Chem. Soc., **45**, 715 (1923).

0.4 cc. of 0.1 N titrating solution of the end-point, then began slowly to decrease, and at the neutral point a clear, sharp downward break occurred. With the reversed titration a rise preceded the end-point which was marked by an upward break of about 100 millivolts. A slight excess of the acid caused the voltage to fall. In neither case was the end-point permanent." In both cases the point of maximum velocity of potential change was exactly at $p_H$ 6.8.

In the authors' opinion, the addition of hydrogen peroxide probably makes the system an oxidation-reduction system, the potential of which depends upon the hydrogen-ion concentration.

Instead of the polarized system, J. C. Brünnich[43] employs a cell composed of a platinum and a graphite electrode. Pure graphite must be used; electric-light carbon is quite unsuitable.

"The combined electrodes were made from a graphite rod about 3 cm. long, enclosed in a glass tube leaving about 2 cm. projecting. A few drops of mercury inside the tube make the connection with a copper wire attached to the positive side of the galvanometer. The glass tube with the graphite rod was enclosed in a wider glass tube, at the lower end of which a few holes were blown to insure ready circulation of the liquid. Around this outer tube a platinum wire was wound and connected with a copper wire to the positive side of the galvanometer."

Brünnich used the potentiometer in all of the tests, but remarks that it is unnecessary for practical purposes and that the electrodes can simply be connected with a sensitive galvanometer giving a distinct deflection with a potential of 2 to 3 millivolts. (Depends also on the current!) "On dipping the electrodes into various solutions, the galvanometer at once indicates their reaction."

"The electrodes are easily affected and the potential of the cell is easily altered, but they are readily tested by successive immersion in three beakers, one containing distilled water, the second one drop of 0.1 N acid, and the third one drop of 0.1 N alkali in 40 cc. of distilled water. The galvanometer must give a strong deflection to the positive side with the acid, and to the negative side with the alkali, and show no deflection in pure water.

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[43] J. C. Brünnich, J. Ind. Eng. Chem., **17**, 631 (1925).

" If kept in contact for any length of time, the tapping key lowers the potential, 0.01 N acid being lowered from 0.18 to 0.10 volt, but again restored to normal after 70 seconds' rest." (Depolarization.) " Temperature slightly alters the potential, 0.01 N acid showing 0.0765 at 6° C.,[44] 0.180 at 22° C., and 0.190 at 42° C."

" The curves of the potentials obtained during titration are quite as characteristic and sharp as those obtained with the hydrogen electrode and calomel cell, although the actual voltage is much lower."

Brünnich used his system for the titration of strong acids and of phthalic, lactic, citric, acetic, phosphoric, and boric acids, and borax. The neutral point is at practically zero difference of potential (− 0.005 volt).

**3. Higher Oxide Electrodes.**—A study of the use of oxide and higher oxide electrodes in hydrogen-ion concentration measurements has recently been published by H. C. Parker.[45] He found that a platinized gold or platinum electrode in contact with manganese sesquioxide ($Mn_2O_3$) was the most satisfactory of a number of electrodes which he tested. In this instance we may be dealing with the reaction:

$$Mn_2O_3 \text{ (solid)} \rightleftarrows 2MnO \text{ (solid)} + \tfrac{1}{2}O_2 \text{ (gas)}.$$

According to Parker, " In alkaline solution it is more likely

$$2Mn(OH)_3 \text{ (solid)} \rightleftarrows 2Mn(OH)_2 \text{ (solid)} + H_2O + \tfrac{1}{2}O_2,$$

and the essential reaction is therefore,

$$Mn^{+++} + e \rightleftarrows Mn^{++}.$$

If the reaction is reversible we may apply Peters' equation, and at 25° C. we should have:

$$E = \varepsilon_0 - 0.0591 \log \frac{[Mn^{++}]}{[Mn^{+++}]} - 0.0591 p_H.$$

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[44] Probably should read 0.1765.

[45] H. C. Parker, J. Ind. Eng. Chem., **17**, 737 (1925).

If the ratio $\frac{[\mathrm{Mn}^{++}]}{[\mathrm{Mn}^{+++}]}$ remains constant, the electrode potential is a linear function of the reciprocal of the hydrogen-ion concentration. . . ."

When the ratio is constant we may write

$$E = \varepsilon_0' - 0.0591 p_H.$$

Parker tested a number of possible electrode combinations in addition to that mentioned above, namely, the following oxides: Manganese dioxide, cobaltic oxide, lead peroxide, hydrogen peroxide, nickelous oxide. These oxides were studied when in contact with one of the following metals: platinum (bright or black), gold (bare or platinized), tungsten, mercury, copper, palladium, nickel; or with carbon. He also studied electrodes of tungsten, nickel, aluminum, copper, palladium, gold, or platinum, without addition of oxide.

Parker determined the $\varepsilon_0$ value of a number of the more promising electrodes by testing them against the hydrogen electrode in various buffer solutions; his values are given in the following table.

$\varepsilon_0$ VALUES OF VARIOUS ELECTRODES AS DETERMINED BY PARKER

| Electrode | Buffer Solution | | | |
|---|---|---|---|---|
| | Phthalate, $p_H=3.92$ | Phosphate, $p_H=6.35$ | Borate $-$NaCl, $p_H=8.25$ | Borate, $p_H=9.07$ |
| $W-Co_2O_3$ | 0.387 | 0.480 | 0.501 | 0.508 |
| $W-MnO_2$ | 0.448 | 0.448 | 0.512 | 0.516 |
| $W-Mn_2O_3$ | 0.402 | 0.486 | 0.501 | 0.502 |
| $W-Mn_2O_3$, treated * | 0.450 | 0.462 | 0.466 | 0.464 |
| W$-$bare | 0.371 | 0.410 | 0.457 | 0.453 |
| W$-$treated * | 0.355 | 0.410 | 0.435 | 0.433 |
| $Pt—Mn_2O_3$ | 0.981 | 1.016 | 1.015 | 1.016 |
| Pt, platinized | 0.928 | 0.940 | 0.945 | 0.940 |
| Pt, platinized$-Co_2O_3$ | 0.918 | 0.952 | 0.952 | 0.954 |
| Au, platinized$-Mn_2O_3$ | 0.965 | 0.976 | 0.971 | 0.967 |
| Pt, platinized$-Mn_2O_3$ | 0.968 | 0.974 | 0.970 | 0.969 |

* The treatment consisted in immersion of the electrode in strongly alkaline buffer solution until the potential became constant (after several days). The effect of the treatment persists for about two weeks when the electrode is used for measurements in a flowing solution.

From Parker's $\varepsilon_0$ measurements it is evident that a number of the electrodes are suitable for use in alkaline solutions, but that the manganese sesquioxide is the only one that is suitable in both acid and alkaline solution. The advantages which are claimed for the use of these electrodes in industrial measurements are: " They can be used in a flowing solution which is freely exposed to air; they require no supply of gas under pressure; they are remarkably free from ' poisoning.' "

If lead peroxide is electrolytically deposited on a platinum electrode, the latter behaves as a lead peroxide electrode, the potential of which depends to a great extent upon the hydrogen-ion concentration. This may be shown by the equation:

$$PbO_2 + 4H^+ + 2e \rightleftarrows Pb^{++} + 2H_2O$$

from which we have:

$$\frac{[Pb^{++}]}{[PbO_2][H^+]^4} = K,$$

and as $[PbO_2]$ is a constant,

$$\frac{[Pb^{++}]}{[H^+]^4} = K'.$$

We have seen from the equation above that two electrons participate in the reaction; the potential of the electrode is therefore represented by the equation:

$$E = \frac{0.059}{2} \log \frac{K[Pb^{++}]}{[H^+]^4} = \varepsilon_0 + \frac{0.059}{2} \log [Pb^{++}] - 0.118 \log [H^+].$$

The more acid the solution the more positive the electrode will be. If the lead-ion concentration could be kept unchanged, the potential of the electrode would change 2 × 59 millivolts with each unit of variation in $p_H$, whereas the hydrogen electrode only changes 1 × 59 millivolts. In a preliminary investigation (not yet published), Kolthoff determined the potential of the lead peroxide electrode in acid and alkaline buffer mixtures. In contrast to the equation above, the potential changed about 130 millivolts for each unit change in $p_H$ of acid solution, and in alkaline solution only 75 millivolts for the same change in $p_H$. The discrepancy has not yet been cleared up.

Kolthoff used a platinum gauze electrode on which lead peroxide was deposited electrolytically (anode in electrolysis of a lead salt in dilute nitric acid). One advantage is that the potential of the electrode soon becomes constant, so that a titration may be finished in a few minutes' time. Its application is limited to the titration of strong oxidants. Good results were obtained in the titration of nitric, perchloric, and chloric acid, of acid in presence of permanganate or dichromate, etc. Hydrochloric acid, however, is oxidized to chlorine and the lead peroxide is dissolved. The electrode then acts as an oxygen electrode.

**4. The Quinhydrone Electrode.**—Since the quinhydrone electrode is a very simple and convenient one for the accurate measurement of the hydrogen-ion concentration in acid solution, and as it has been applied more and more frequently for this purpose, a rather detailed discussion of it will be given here.

If we have a reversible oxidation-reduction reaction which may be represented by the equation:

$$A + 2H^+ + 2e \rightleftarrows H_2A,$$

the oxidation potential of the system will be:

$$E = \varepsilon_0 + \frac{0.059}{2} \log \frac{[A][H^+]^2}{[H_2A]},$$

or

$$E = \varepsilon_0 + \frac{0.059}{2} \log \frac{[A]}{[H_2A]} + 0.059 \log [H^+] \quad (25°).$$

This relation has been confirmed for the systems: hydroquinone-quinone (Biilmann); dialuric acid-alloxan (Biilmann and Lund); azo-hydrazo compounds (Biilmann); cystine-cysteine (Dixon and Quastel, 1923). Of these systems the quinone-hydroquinone one is the most suitable for practical use, as the two substances unite in equimolecular proportions to form the slightly soluble compound, quinhydrone.

The quinhydrone electrode has a certain hydrogen pressure which is very small; its magnitude is regulated by the reaction:

$$\underset{\text{quinone}}{C_6H_4O_2} + H_2 \rightleftarrows \underset{\text{hydroquinone}}{C_6H_4O_2H_2}.$$

The hydrogen concentration in the electrode is equal to:

$$[H_2] = K\frac{[\text{hydroquinone}]}{[\text{quinone}]}.$$

The hydrogen pressure is so small that it is hardly capable of practical realization (at 18° and $p_H = 0$, $P_{H_2} = 10^{-24.4}$). The authors therefore prefer to represent the transformation of quinone into hydroquinone by the electrochemical equation:

$$C_6H_4O_2 + 2H^+ + 2e \rightleftarrows C_6H_4O_2H_2.$$

Two hydrogen ions are discharged in this reduction. The potential of the electrode will therefore be:

$$E = \frac{0.059}{2}\log\frac{K[\text{quinone}][H^+]^2}{[\text{hydroquinone}]} \quad (25°).$$

As quinhydrone is an equimolecular compound of quinone and hydroquinone, we have:

$$[\text{quinone}] = [\text{hydroquinone}],$$

and

$$E = \frac{0.059}{2}\log K[H^+]^2 = \varepsilon_0 + 0.059 \log [H^+].$$

Hence the quinhydrone electrode changes its potential in exactly the same way, with changes in hydrogen-ion concentration, as the hydrogen electrode does.

According to E. Biilmann[46] and his collaborators, at 18°

$\varepsilon_0 = 0.7044$ volt (referred to normal hydrogen electrode).

According to E. Biilmann and J. Krarup,[47] the temperature coefficient of the cell: quinhydrone electrode — normal hydrogen electrode, between 0° and 37°, is equal to $-0.00074$ volt. From the aforesaid and the data in the literature, we find:[48]

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[46] E. Biilmann, Ann. de chimie (9), **15**, 109 (1921); E. Biilmann and H. Lund, Ann. de chimie, **16**, 321 (1921); **19**, 137 (1923); E. Biilmann, Trans. Faraday Soc., **19**, 57 (1923).

[47] E. Biilmann and J. Krarup, J. Chem. Soc., **125**, 1954 (1924).

$$p_{\mathrm{H}} = \frac{0.3665 - 0.00068(t - 18) - \pi_{0.1\mathrm{N}}}{0.0577 + 0.0002(t - 18)},$$

$\pi_{0.1\mathrm{N}}$ = E.M.F. against the 0.1N calomel electrode.

$$p_{\mathrm{H}} = \frac{0.4181 - 0.00050(t - 18) - \pi_{1\mathrm{N}}}{0.0577 + 0.0002(t - 18)},$$

$\pi_{1\mathrm{N}}$ = E.M.F. against the N calomel electrode.

$$p_{\mathrm{H}} = \frac{0.4496 - 0.00035(t - 18) - \pi_{3.5\mathrm{N}}}{0.0577 + 0.0002(t - 18)},$$

$\pi_{3.5}$ = E.M.F. against 3.5 N calomel electrode.

The quinhydrone electrode furnishes us with a rapid means for the determination of hydrogen-ion concentrations. Its manipulation is much more convenient than that of the hydrogen electrode. The electrode is a bright piece of platinum wire, foil, or gauze. In order to make the electrode ready for use, the electrolyte is shaken for about half a minute with a little quinhydrone (about 50–100 mg.) and then the measurement can be made. The electrode must be cleaned, if necessary. The quinhydrone may be very suitably prepared as follows: 100 g. ferric ammonium sulphate are dissolved in 300 cc. water at 65° C., and this solution is poured into a solution of 25 g. hydroquinone in 300 cc. water. The quinhydrone precipitates in fine needles; after cooling in ice it may be collected by suction. Yield, 15 g. After recrystallization from water it contains only a trace of iron.

The quinhydrone electrode may often be applied in cases where the hydrogen electrode does not give good results, as in the presence of metals that lie below hydrogen in the electromotive series; also in the presence of alkaloids. It may be applied to the determination of the acidity of soils,[49] or of milk and dairy products.[50] It is also important from a theoretical point of view.[51] Its salt error has been determined by S. P. L. Sörensen and his collaborators;[52] the protein error by Kolthoff (*loc. cit.*).

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[48] *Cf.* I. M. Kolthoff, Z. physiol. Chem., **144**, 259 (1925).

[49] I. M. Kolthoff, Rec. trav. Chim., **42**, 186 (1923); E. Biilmann, J. Agric. Science, **14**, 232 (1924); H. R. Christensen and S. J. Jensen, Internat. Mitt. f. Bodenk., **14**, Heft I–II (1924).

One serious objection to the application of the quinhydrone electrode is that it can not be used in alkaline solution. The hydroquinone acts as a weak acid and gives off hydrogen-ions, and incorrect values for $p_H$ are found. In general we may say that when $p_H$ is smaller than 8 reliable results are obtained. In solutions of good buffer capacity good results are obtained even at $p_H = 9$.

The quinhydrone electrode can be warmly recommended for titrations.[53] If we wish to carry out a titration some quinhydrone is added to the solution and a platinum electrode is dipped in. Electrical stirring is usually unnecessary, for the electromotive force rapidly becomes constant upon stirring by hand with a glass rod. It is very convenient for the titration of acids, or of salts of weak acids with strong acids. It has been applied by Kolthoff (*loc. cit*), Baggergeard-Rasmussen (*loc. cit.*), and Wagener and McGill (*loc. cit.*) to the titration of alkaloids and their salts. Harris (*loc. cit.*) employed the electrode in the titration of amino acids. It may also be used in the determination of the acidity of beverages, fruit juices, soils, etc.

As we have seen, the quinhydrone electrode gives unreliable results in alkaline solutions. This, however, would not influence the result of a titration if it were not for another objectionable feature, namely, that the hydroquinone is readily oxidized in such solutions to form brown-colored weak acids which neutralize part of the base. This causes a negative error which may be appreciable. Kolthoff (*loc. cit.*) stated: If the air is removed, and the titration carried out in a nitrogen atmosphere, good results are obtained. It is more convenient to add an excess of acid to the alkaline solution and titrate back with standard sodium hydroxide. If the solution to be titrated contains strong oxidants or reductants the quinhydrone electrode is no longer applicable, nor is the hydrogen electrode. In some cases the quino-quinhydrone electrode (quinhydrone and quinone) may be used.

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[50] V. Lester, J. Agric. Science, **14**, 634 (1924).

[51] J. S. Granger, Dissertation, New York (1920); J. S. Granger and J. M. Nelson, J. Am. Chem. Soc., **43**, 1401 (1921); J. B. Conant, H. M. Kahn, L. J. Lieser, and S. S. Kurts, *ibid.*, **44**, 1382 (1922); J. B. Conant and L. J. Lieser, *ibid.*, **44**, 2480 (1922); **45**, 2194 (1923); V. K. La Mer and L. E. Baker, *ibid.*, **44**, 1954 (1922); L. E. Baker, Dissertation, New York (1922); E. Biilmann, A. L. Jensen, and K. O. Pedersen, J. Chem. Soc., **127**, 199 (1925).

[52] S. P. L. Sörensen, M. Sörensen, and K. Linderström-Lang, Ann. de Chimie, **15**, 111 (1921); K. Linderström-Lang, Compt. rend. du Lab. de Carlsberg, **15**, No. 4 (1924).

[53] I. M. Kolthoff, Rec. trav. chim., **42**, 186 (1923); V. K. LaMer and T. R. Parsons, J. Biol. Chem., **67**, 613 (1923); L. J. Harris, Proc. Roy. Soc., **95**, 439, 499 (1923); J. Chem. Soc., **123**, 3294 (1923); J. Auerbach and E. Smolczyk, Z. physik. Chem., **110**, 65 (1924); H. Baggergeard-Rasmussen, Z. Elektrochem., **31**, 189 (1925); L. R. Wagener, and W. J. McGill, J. Am. Pharm. Assoc., **14**, 288 (1925).

Since the potential of the quinhydrone electrode rapidly becomes constant, the Pinkhof system and its modifications may be used advantageously. The solution to be titrated is brought into electrolytic contact with a quinhydrone electrode which is placed in a buffer solution of the same $p_H$ as that at the equivalence point. The reagent is added until the galvanometer or capillary electrometer gives no deflection.

**5. Metal Electrodes.**—The potential between a metal and a solution depends upon the concentration of the ions which the electrode can furnish. Let us assume that we have a metal whose oxide has a very slight solubility. In this case the metal-ion concentration of the solution will be governed by its hydrogen-ion concentration. If we have for example the bivalent metal M whose oxide MO is slightly soluble, then we have:

$$MO + 2H^+ \rightleftarrows M^{++} + H_2O$$

$$[M^{++}] = K[H^+]^2$$

as the concentration of MO is a constant.

From the Nernst equation, we have:

$$E = \varepsilon_0 - \frac{0.059}{2} \log [M^{++}],$$

and as we may write $K[H^+]^2$ in place of $[M^{++}]$, we have

$$E = \varepsilon_0 - \frac{0.059}{2}\log K - \frac{0.059}{2}\log [H^+]^2$$

$$= \varepsilon'_0 - 0.059 \log [H^+].$$

It may be concluded from the last equation that the electrode potential varies in the same way with changes in hydrogen-ion concentration as does the hydrogen electrode. This conclusion, of course, holds only when we may assume that the solubility of the oxide is so small at the various hydrogen-ion concentrations that it does not affect the latter.

If we have a trivalent metal the oxide of which is very slightly soluble, an equation similar to the above may be derived. Actually, only a few metals may be used as indicator electrodes for hydrogen ions, since the particular metal must be less electropositive than hydrogen. Also, if we are to use the electrode over the whole range, its oxide must be insoluble in both acids and bases. One of the few metals that fulfill these conditions is antimony, the oxide of which is amphoteric.

*The Antimony Electrode.*—The solubility of the oxide is so small, even in 0.1 N hydrochloric acid and 0.1 N sodium hydroxide, that it does not change the hydrogen-ion concentration of these liquids. In view of the results of K. Schuhmann,[54] we may conclude that in dilute acid solutions the antimony trioxide goes into solution with the formation of antimonyl ions, $SbO^+$:

$$Sb_2O_3 + 2H^+ \rightleftarrows 2SbO^+ + H_2O.$$

As the potential of the anitmony electrode is dependent upon the $SbO^+$ concentration, and the latter is determined by the hydrogen-ion concentration, it is obvious that the potential of the antimony electrode will change in the same manner as the hydrogen electrode does. It is true that I. M. Kolthoff and B. D. Hartong [55] in a preliminary paper have found that this conclusion does not hold exactly; the deviation is rather large in acid solution. At 14° C. they found that up to $p_H$ of 5 in acid solution the E.M.F. changes 48.5 millivolts for each unit of change in $p_H$, whereas in alkaline solution at $p_H$ above 9 it changes 53.6 millivolts for a variation of 1 in $p_H$. The behavior of the antimony electrode has not yet been satisfactorily explained from a theoretical point of view. Yet it is suitable for analytical neutralizations, and may be used in many cases where the hydrogen electrode is not applicable.

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[54] K. Schuhmann, J. Am. Chem. Soc., **46**, 52 (1924).

[55] I. M. Kolthoff and B. D. Hartong, Rec. trav. chim., **44**, 113 (1925).

The antimony electrode was first used for this purpose by Uhl and Kestranek,[56] whereas Kolthoff and Hartong (*loc. cit.*) made an extensive study of its properties. The latter used antimony obtained from Kahlbaum (99.97 per cent Sb), which was melted and poured into a cylindrical mould. The rod so obtained was joined to a copper wire which was connected to the circuit. According to Uhl and Kestranek the antimony contains enough antimony oxide so that it may be used directly without any addition. Kolthoff and Hartong found that more reliable results and more rapidly constant potential were obtained if a little antimony trioxide was added. This is not necessary for ordinary titrations, but if it is desired to calculate the $p_H$ corresponding to the measured E.M.F. the presence of some oxide is essential. The latter may easily be obtained by treating antimony with sufficient nitric acid, evaporating to dryness, and gently igniting the residue.

In order to obtain good results the liquid must be stirred during the titration, by a motor stirrer or by a current of indifferent gas such as hydrogen or nitrogen. The E.M.F. generally reaches a constant value within two minutes. The results of various titrations are very satisfactory: hydrochloric, sulphuric, nitric, perchloric, acetic, oxalic, and some other acids were titrated successfully. A good result was also obtained with tartartic acid, although the E.M.F. did not correspond to the $p_H$ of the solution. The deviation must be ascribed to the formation of the complex antimonyl tartrate. As a consequence, the break is not as large as in the case of oxalic acid. There is also a measurable quantity of antimony trioxide in the liquid after the titration of the tartaric acid.

[56] Uhl and Kestranek, Monatsh., **44**, 29 (1923).

Conversely, alkaline solutions may also be successfully titrated with acid. The antimony electrode may also be used in many cases where the hydrogen electrode is used (e.g., in the titration of beer). It may even be used in cases where the hydrogen electrode interferes, as in the titration of alkaloids. It gives good results in the presence of strong oxidzing agents, such as permanganate or dichromate, although the E.M.F. observed does not correspond with the hydrogen exponent of the solution. Thus, for example, the antimony electrode was strongly positive against the normal calomel electrode in a solution that contained 0.05 N sulphuric acid and 0.05 N permanganate. After neutralization of practically all of the acid, the E.M.F. fell to zero and changed sign with respect to the calomel electrode. As the permanganate oxidizes the trivalent antimony to the quinquivalent condition, the anomaly is explained by the fact that we are dealing with the $Sb\text{–}Sb^{V}$ electrode instead of the $Sb\text{–}Sb^{III}$ as in other cases. Still, the acid in the permanganate or dichromate can be determined accurately. In the latter case, the first break in potential is at a point corresponding to dichromate, the second to chromate.

A more systematic investigation of the antimony electrode is desirable.

*The Mercury-Mercuric Oxide Electrode*:

$$Hg(OH)_2 \rightleftarrows Hg^{++} + 2OH^-,$$

$$[Hg^{++}][OH^-]^2 = S_{Hg(OH)_2},^{57}$$

$$[Hg^{++}] = \frac{S_{Hg(OH)_2}}{[OH^-]^2},$$

$$E_{Hg} = \varepsilon_0 - \frac{0.059}{2}\log[Hg^{++}] = \varepsilon_0 - \frac{0.059}{2}\log\frac{S_{Hg(OH)_2}}{[OH^-]^2},$$

$$E_{Hg} = \varepsilon_0' + 0.059\log[OH^-].$$

The mercury-mercuric oxide electrode is an indicator for hydroxyl ions and changes its potential in the same manner

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[57] According to I. M. Kolthoff, Chem. Weekblad, **14**, 1016 (1917), $S_{Hg(OH)_2}$ is equal to $1.4 \times 10^{-26}$ at (18° C.).

with hydroxyl-ion concentration as the hydrogen electrode does. This electrode can not, of course, be used in acid solutions, because the mercuric oxide dissolves. Another objection is that mercuric ions react with mercury to form mercurous ions:

$$Hg^{++} + Hg \rightleftarrows Hg_2^{++}.$$

This reaction may occur even at small hydrogen-ion concentrations, and black mercurous oxide is precipitated. The limit of $p_H$ to which the Hg–HgO electrode may be used depends very largely upon the chloride-ion content of the solution. The chloride ions remove the mercurous ions from the solution, forming calomel, and the above reaction is shifted to the right. Other halides also have a disturbing action. J. Pinkhof [58] gives the following table:

| $[Cl^-]$ | $[OH^-]$ at which Reduction Occurs | $[H^+]$ at which Reduction Occurs |
|---|---|---|
| 1 | $10^{-3}$ | $10^{-11}$ |
| $10^{-1}$ | $10^{-4}$ | $10^{-10}$ |
| $10^{-2}$ | $10^{-5}$ | $10^{-9}$ |
| 0 | $10^{-6}$ | $10^{-8}$ |

When the chloride concentration is smaller than 0.01 N, black mercuous oxide will be formed as soon as the hydrogen-ion concentration becomes larger than $10^{-8}$. Hence, it is only possible to make those tirations of which the $p_H$ at the equivalence-point is larger than 8. At higher chloride concentrations, the $p_H$ must be proportionately higher (*cf.* table). The application of the mercury-mercuric oxide electrode is therefore very limited. In the authors' opinion, the antimony electrode is better, because fewer substances interfere with its use, and it may also be used in acid media. Pinkhof gives some applications of the mercury-mercuric oxide electrode, which will be mentioned briefly.

*Titration of Ammonia in its Salts.*—The solution which is to be titrated must be about 1 N. An excess of normal sodium hydroxide is added, and is then determined with normal nitric acid. Compensation electrode, Hg–HgO in 0.1 N NaOH. A correction of 0.15 cc. of 0.1 N NaOH has to be added to the number of cubic centimeters of alkali bound per 10 cc. of solution. This titration is of little more than theoretical interest. The sharpest change in potential occurs at a sodium hydroxide concentration of 0.15 N. Pinkhof takes this as the end-point, and corrects for the excess of alkali. The value of the potential is not the same as in pure alkali. This fact is explained by the transformation of the mercuric oxide into the Millon base, $(HgOH)_2NH_2OH$, by the ammonia. In normal ammonia this base has a mercuric-ion concentration about 100 times smaller than mercuric oxide at the same hydroxyl-ion concentration, and therefore in the former case the electrode potential is about 58 millivolts less negative than in the absence of ammonia. Inflection-potential, − 0.100 volt against normal calomel electrode. The authors can not recommend this titration for practical use.

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[58] J. Pinkhof, Dissertation, Amsterdam (1919), p. 31.

*Titration of Magnesium in the Presence of Calcium.*—(*Cf.* p. 209.) An excess of normal sodium hydroxide is added to the solution to be titrated, the magnesium concentration of which may not be less than 0.5 N. Chloride and sulphate ions must be absent. The excess of alkali is determined with normal nitric acid. Compensation electrode, normal calomel electrode. (Inflection-potential, 0.00 volt.) This method is of little practical use.

Pinkhof also uses the Hg–HgO electrode for the titration of phosphates, pyrophosphates, and boric acid. Heavy metals can not be titrated with an excess of sodium hydroxide because of the adsorbing action of the hydroxide formed. Alkaloids in their salts may be titrated in the same way as magnesium and ammonium. The titration may be carried out even in 0.05 N solutions. Not even the presence of 0.05 N chloride is harmful. An excess of sodium hydroxide is added, and the amount of the excess is determined with acid. Compensation electrode, 0.1 N calomel electrode. (Inflection-potential, + 0.050 volt against normal calomel electrode.) Accuracy about 1 per cent.

The titration of morphine is less accurate, owing to the acid character of the free alkaloid, which is a phenol.

The authors suggest that the copper-cupric oxide electrode might have a wider field of application than the Hg–HgO electrode. Thus far, no data are available to prove this surmise. (*Cf*. Parker, J. Ind. Eng. Chem. **17,** 737 (1925)).

**6. The Tungsten Electrode.**—J. R. Baylis[59] found that the tungsten wire in an ordinary 40-watt electric lamp is an indicator for hydrogen ions. In his experiments he used the water of Gunpowder River, the $p_H$ of which ranged between 6.5 and 8.6. The useful range may not extend much beyond these limits. (*Cf*. Parker, *loc. cit.*) There is a voltage difference of approximately 90 millivolts for each $p_H$ unit (hydrogen electrode, 59 millivolts). Baylis tested only water from the one source. A hole large enough to admit two small tubes was bored in the lamp bulb. One tube led from the calomel electrode, the other from the water source. A rapid displacement of water gave the best results. A lamp gave accurate readings for about a week, after which gradual deviations from the first readings occurred. Baylis' paper was of preliminary character, and a more systematic investigation over a wider $p_H$ is highly desirable. The results obtained by Parker (*loc. cit.*) show that the electrode does not change regularly with $p_H$ changes throughout the whole range.

The authors suggest that the tungsten electrode behaves more or less as an oyxgen electrode.

**7. The Glass Electrode.**—We may use a glass electrode instead of a metal electrode. Haber and Klemensiewicz[60] found that the potential difference between electrolytes in contact with the two sides of a thin glass wall is determined in part by the hydrogen-ion concentration of the solution. Within the the last few years, K. Horovitz and his collaborators have, as a matter of fact, shown that the glass electrodes behave as mixed electrodes. Their potential depends not only upon the hydrogen-ion concentration, but also upon that of the other ions which the glass contains (e.g., zinc, sodium, etc.). Horovitz gives many details regarding the neutralization curves, which will not be discussed here.

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[59] J. R. Baylis, Ind. Eng. Chem., **15**, 852 (1923).

[60] Haber and Klemensiewicz, Z. physik. Chem., **67**, 385 (1909).

Haber's apparatus is illustrated in Fig. 42.

S is the solution to be titrated, B a glass bulb with walls 0.06 mm. thick, and filled with potassium chloride solution; W is a platinum wire which dips into the potassium chloride solution; E is a quadrant electrometer, C a standard half-cell (calomel electrode). According to Haber, the potential difference between the interior of the glass forming the bulb and the solution outside varies linearly with the $[H^+]$ of solution S. (*Cf.* Horovitz.) Haber suggested that the variation in contact potential might be made the basis of an electrometric titration.

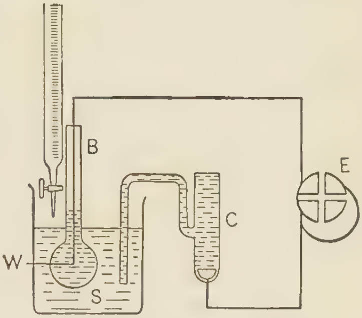

FIG. 42.—Glass cell (Haber).

W. S. Hughes[61] used a Leeds and Northrup potentiometer and compensated until the quadrant electrometer gave no deflection. According to Hughes, multivalent cations and anions have no influence on the potential difference between glass and solution. In the titration of gelatin, however, they have a marked influence.

The reader is referred for details to the paper of Hughes (*loc. cit.*) and Horovitz.[62] In the authors' opinion, glass electrodes are of no practical importance in analytical titrations, because we have a choice of so many electrodes which may be used with simple equipment. There is, however, another phase of the matter which might be of importance. Horovitz found that a glass electrode behaved as a sodium electrode and also as a zinc electrode when the glass contained zinc. Therefore, it might be possible to use these glass electrodes in cases where metal electrodes can not be employed (calcium, barium, lead, etc.). If this were the case, there would be a broad field for extensive and important research.

[61] W. S. Hughes, J. Am. Chem. Soc., **44**, 2860 (1922). *Cf.* also A. L. v. Steiger, Z. Elektrochem., **30**, 259 (1924). *Cf.* W. E. L. Brown, J. Sci. Insts., **2**, 12 (1924).

[62] *Cf.* H. Freundlich, Kapillar Chemie (1923) regarding contact potentials.

## CHAPTER XI

## OXIDATION-REDUCTION REACTIONS

As we have seen in Part I, many oxidation-reduction reactions in which hydrogen ions play a part are not completely reversible, probably because of the formation of intermediate products. Therefore, in many cases, we must be careful not to lay too much stress on the values for the normal potentials of these oxidation-reduction systems, because they often represent the potential value of the system under special conditions. We often observe characteristic properties of a system, as, for example, the influence of chromic chromium on the chromic acid-chromic ion potential, which are not easily explained theoretically.

In this chapter the authors will describe the titrations that may be carried out with various oxidants and reductants as reagents. The application of one oxidant or reductant will be given in each section. This may involve the disadvantage that the estimation of individual substances (e.g., iodide, etc.) is described in several sections. The authors nevertheless prefer this method to others for a systematic treatment of the subject.

**1. Titrations with Potassium Permanganate.**—A 0.1 neutral solution of potassium permanganate, if free from manganese dioxide and protected from dust and other foreign matter, may be preserved for a long time without changing its strength. More dilute solutions must be standardized every time they are used. The standardization may be made with the usual primary standards by the ordinary methods, or by potentiometric titration.[1]

According to F. Crotogino,[2] the accurate measurement of the oxidation potentials of oxidants, which may furnish oxygen, is impossible. He used platinized electrodes, which Kolthoff also used in his earlier work on potentiometric titrations. Kolthoff afterward found that bright platinum electrodes gave far more constant potential values. With the bright electrode,

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[1] *Cf.* I. M. Kolthoff, Z. anal. Chem., **64**, 255 (1924).

[2] F. Crotogino, Z. anorg. Chem., **24**, 224 (1900).

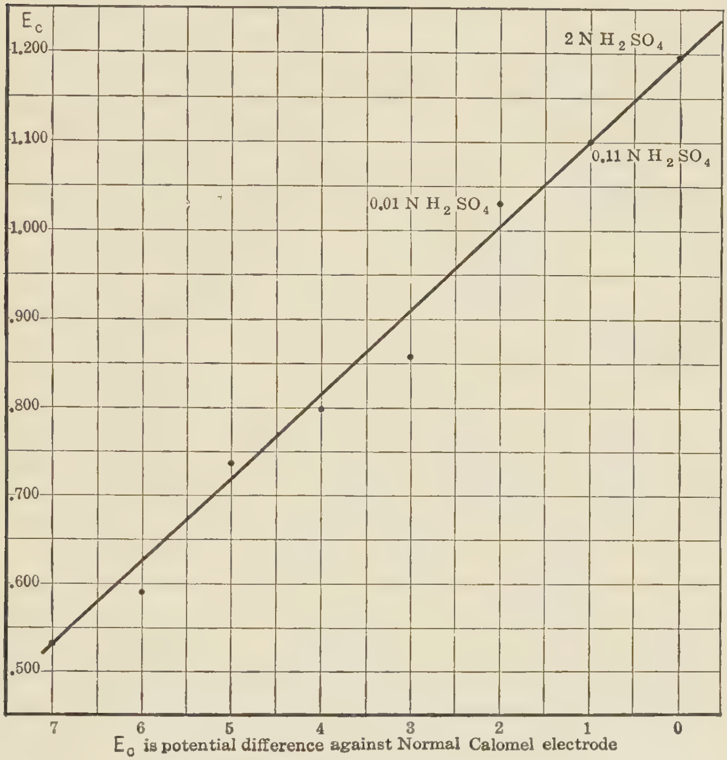

FIG. 43.—Potential of 0.01 N $KMnO_4$ at various $p_H$.

Kolthoff determined the permanganate potential at various values of $p_H$. Buffer mixtures were used up to a $p_H$ of 2, then 0.01 N, 0.12 N, and 2 N sulphuric acid was used. The results are plotted in the curve of Fig. 43.

It may be seen that not all of the points lie on a straight line. It is possible, however, that the buffer mixtures from 6 to 3 (Clark mixtures) react with the permanganate to some extent. A phosphate mixture was used at $p_H = 7$. In this solution ($p_H = 7$) the potential was 0.530 volt against the normal calomel electrode; in 2 N sulphuric acid of $p_H = 0$, it was 1.193 volt (25°). Hence, for one unit change in $p_H$, there is a variation of 95 millivolts. According to the equation:

$$E = \varepsilon_0 + \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{++}]}$$

the theoretical change is $\frac{8}{5} \times 0.059 = 94.4$ millivolts per each unit change in $p_H$. Hence, the agreement between the theoretical and actual values is satisfactory.

From the potential of 0.01 N permanganate at $[H^+] = 1$, we calculate that a 1 N solution at $[H^+]=1$ will have a potential of 1.217 volts against the normal calomel electrode, or of 1.503 volts against the normal hydrogen electrode.

*Titration of Iodide*:

$$MnO_4^- + 8H^+ + 5I^- \rightleftarrows Mn^{++} + 4H_2O + 2\tfrac{1}{2}I_2.$$

Partial reactions:

$$MnO_4^- + 8H^+ + 5 \ominus \rightleftarrows Mn^{++} + 4H_2O;$$

$$\varepsilon_0 = 1.217 \text{ volt (against N.C.E.)}^3$$

$$5I^- \rightleftarrows 2\tfrac{1}{2}I_2 + 5 \ominus$$

$$\varepsilon_0 = 0.346 \text{ (N.C.E.)}$$

The electrometric titration of iodides was first described by Crotogino (*loc. cit.*) who titrated in a solution which contained 0.1 N sulphuric acid. W. S. Hendrixson[4] showed that the method gave very accurate results, and this was confirmed by I. M. Kolthoff.[5] The accuracy is so great that pure potassium iodide may be recommended as a primary standard for establishing the normality of potassium permanganate solutions. Kolthoff used pure potassium iodate for this purpose; the reduction was performed with pure sulphurous acid, the excess of

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[3] Hereafter the authors will use N. C. E. as abbreviation for normal calomel electrode.

[4] W. S. Hendrixson, J. Am. Chem. Soc., **43**, 14 (1921).

[5] I. M. Kolthoff, Rec. trav. chim., **40**, 532 (1921).

which was boiled off. Crotogino (*loc. cit.*) did not obtain accurate results. As Kolthoff (*loc. cit.*, 1921) showed, the acidity of his solutions was too slight. The liquid must contain enough sulphuric acid to make it 0.15 N; it is better to titrate in solutions that are 0.2 – 0.5 N with respect to acid. At very low acid concentration, the jump in potential appears too late.

The potential is very constant during the titrations. Motor stirring is unnecessary. Stirring with a current of air or carbon dioxide is satisfactory. The potential assumes a constant value more slowly just at the equivalence-point, and a wait of about one minute is necessary, until a steady value is found. After all of the iodine has been liberated, the excess of permanganate oxidizes it slowly to iodate. Hence, after addition of reagent the potential is strongly positive, but falls again because of the oxidation of the iodine. As the jump in potential at the equivalence-point is so large, a small error in the determination of the potential has no influence at all on the result. Even very dilute iodide solutions may be accurately analyzed by means of the permanganate titration. E. Müller and H. Möllering[6] titrate to an inflection-potential of + 0.64 volt (against N.C.E.). The solution contained 0.8 N sulphuric acid. According to their results, 1 per cent too much permanganate is used if one waits until the potential is constant. This conclusion is not warranted as Hendrixson and Kolthoff (*loc. cit.*) showed. On the contrary, the iodide titration of permanganate is one of the most accurate that we have.

In the presence of increasing amounts of bromide the voltage rise at the end-point becomes progressively less abrupt. When the amount of bromide exceeds that of iodide by 25 per cent the results are high (Hendrixson). Kolthoff was able to titrate iodide in the presence of double the amount of bromide with an accuracy of 0.5 per cent. With more bromide the end-point becomes uncertain.

Chloride interferes much less with the result of the titration, although the potential curve at the end-point becomes less steep. With a ratio $I^- : Cl^-$ of 1 : 20 accurate results are still obtained.

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[6] E. Müller and H. Möllering, Z. anorg. Chem., **141**, 111 (1924).

In the presence of hydrochloric acid an excess of permanganate reacts with iodine according to the equation (Müller and Möllering):

$$MnO_4^- + 8H^+ + 5I + 5Cl^- \rightleftarrows Mn^{++} + 5ICl + 4H_2O.$$

The break in potential in the titration of iodide solutions is much greater when cyanide is also present. R. Lang [7] published a number of papers in which he recommended a new method of iodometry applicable in the presence of a weak acid. In titrating iodide in the presence of HCN the end-point is not obtained when all of the iodine is liberated, but at the point where all of the iodine is transformed into ICN. The following equation represents the reaction:

$$2MnO_4^- + 11H^+ + 5I^- + 5HCN \rightleftarrows 2Mn^{++} + 5ICN + 8H_2O$$

with the partial reactions:

$$2MnO_4^- + 16H^+ + 10\ominus \rightleftarrows 2Mn^{++} + 8H_2O,$$

$$5I^- + 5HCN \rightleftarrows 5ICN + 5H^+ + 10\ominus.$$

Hence twice as much reagent is used at the end-point as in the absence of HCN. The oxidation of the iodide is very rapid and the titration can be finished in five minutes. H. H. Willard and F. Fenwick [8] applied their bimetallic system to the determination of the end-point of this reaction. From their results it may be concluded that the selective oxidation of iodide in hydrocyanic acid solution to iodine cyanide is possible in all concentrations of chloride and in moderate concentrations of bromide. The magnitude of the latter is a function of the ratio of bromide to iodide concentration and of the absolute concentration of each. In cases where these factors are unknown, the authors propose the titration of duplicate samples in dilutions which differ by at least 100 per cent. If the consumption of oxidizing agent is the same in both cases, the results may be regarded as trustworthy. In the authors' opinion the application of the ordinary potentiometer system is advantageous here.

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[7] R. Lang, Z. anorg. Chem., **122**, 332 (1922); **142**, 229,279 (1924); **144**, 75 (1925).

[8] H. H. Willard and F. Fenwick, J. Am. Chem. Soc., **45**, 623 (1923).

Since the iodide titration with permanganate gives such accurate results, W. S. Hendrixson [9] has applied it to the determination of other substances. Iodate is determined by adding an excess of iodide to its acid solution and titrating back with permanganate. (The direct titration of iodate with iodide also gives good results; *vide infra.*) Silver is precipitated by an excess of iodide and the amount of the latter is determined with permanganate. The titration may be made in the presence of the precipitate because of its extremely slight solubility. Metallic silver is dissolved in a small excess of nitric acid; most of the excess is evaporated off. Since the titration gives very accurate results Hendrixson recommends pure silver as a primary standard in determining the normality of iodide or of potassium permanganate.

In a later paper W. S. Hendrixson [10] applied the iodide titration to the determination of bromate, nitrite, and chloride. An excess of iodide solution is added to the bromate solution, which is 2 N with respect to sulphuric acid, and the excess of iodide is determined with permanganate. For the determination of nitrite, permanganate solution is run into the titration vessel, diluted, and enough 10 N sulphuric acid is added to make the final solution 1.5 N. The stirrer is started and the nitrite solution is added slowly in an amount which leaves 5 to 10 per cent of the permanganate unchanged. After about five minutes an excess of iodide is added and the titration is completed with permangante.

In the titration of chloride an excess of silver nitrate is added to the solution; the silver chloride is filtered off and the excess of silver in the filtrate is determined as described above. This method for the determination of chloride is of little practical importance.

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[9] W. S. Hendrixson, J. Am. Chem. Soc., **43**, 858 (1921).

[10] W. S. Hendrixson, J. Am. Chem. Soc., **43**, 1309 (1921).

*Bromide.*—H. H. Willard and F. Fenwick (*loc. cit.*) applied the direct titration of bromide in the presence of hydrocyanic acid:

$$2MnO_4^- + 11H^+ + 5Br^- + 5HCN \rightleftarrows 2Mn^{++} + 5BrCN + 8H_2O.$$

With partial reactions:

$$2MnO_4^- + 16H^+ + 10\ominus \rightleftarrows 2Mn^{++} + 8H_2O,$$

and

$$5Br^- + 5HCN \rightleftarrows 5BrCN + 5H^+ + 10\ominus.$$

The bimetallic system did not give a satisfactory end-point. The usual potentiometric system with a standard half-cell gave a distinct maximum. The break was not " found to be ideal, but offers distinct possibilities, particularly in a case such as this where there is no other method available. After each addition of reagent there is a slight drag before equilibrium is reached." Ignition of the electrode before each titration was found to aid in keeping the end-point rise abrupt.

To 10 cc. of 0.1 N bromide are added 5 cc. 10 per cent potassium cyanide solution, 10 cc. sulphuric acid (sp. gr. 1.84) and water to bring volume to 100 cc. An arbitrary correction of − 0.10 cc. 0.1 N reagent is applied to the value found at the maximum of $\frac{\Delta E}{\Delta c}$. Even in the presence of large amounts of hydrochloric acid the error in the titration never amounted to more than 0.42 mg. of bromide. " A sub-maximum often precedes the end-point maximum in the $\frac{\Delta E}{\Delta c} \sim c$ curve and the intervening sub-maximum lies extremely close to the theoretical end-point." This sub-maximum, however, does not always occur. In the presence of iodide the latter is first oxidized to iodine cyanide, whereupon a sharp break in potential occurs. Further addition of permanganate oxidizes the bromide. If the ratio $I^- : Br^-$ is 1 : 1, good results are obtained. If it is less favorable too much reagent is used for the oxidation of the iodide. In this case Willard and Fenwick oxidize the iodide to iodate with sodium hypobromite. (*Cf.* p. 283.)

*Sulphurous Acid.*—W. S. Hendrixson and L. M. Verbeck [11] added sulphuric acid to the solution to be titrated (final acid concentration 1 N) and an excess of permanganate. This excess is destroyed by a small excess of iodide, which is determined with permanganate. The method does not yield accurate results as the oxidation of the sulphurous acid to sulphate is not quantitative. I. M. Kolthoff [12] confirmed this statement, but found that the oxidation of sulphite to sulphate by permanganate was complete in alkaline medium. An excess of permanganate is added to the alkaline sulphite solution. Sufficient sulphuric acid is then added and the titration is completed according to Hendrixson.

*Oxalate.*—Carlos del Fresno [13] applied the potentiometric method to the titration of oxalate with permanganate. As might be expected, the method gives accurate results at 70°. It has no advantage over the ordinary titration.

*Ferrocyanide*:

$$\mathrm{MnO_4^- + 8H^+ + 5Feoc^{----} \rightleftarrows Mn^{++} + 4H_2O + 5Feic^{---}}.$$

Partial reactions:

$$\mathrm{MnO_4^- + 8H^+ + 5\ominus \rightleftarrows Mn^{++} + 4H_2O};$$

$$(\varepsilon_0 = 1.217,\ \mathrm{N.C.E.})$$

$$\mathrm{5Feoc^{----} \rightleftarrows 5Feic^{---} + 5\ominus};$$

$\varepsilon_0$ depends upon $[\mathrm{H^+}]$.

The potentiometric titration of ferrocyanide gives such accurate results that Kolthoff (1924) has applied it in the standardization of permanganate. G. L. Kelley and R. T. Bohn [14] first used this potentiometric titration. They employed a platinized electrode, while Kolthoff prefers a bright electrode. The jump in potential at the end-point is very large; the more acid there is present, the larger the break at the equivalence-point. There is another reason for carrying out the titration in strongly acid solution. One of the products of the reaction is manganous salt, which may form a precipitate of $K_2MnFeoc$. The precipitate coats the electrode and interferes seriously with the titration. Therefore, according to I. M. Kolthoff [15] the sulphuric acid content of the solution should be rather high in order to prevent this precipitation, and the ferrocyanide concentration should be just less than 0.05 N. Kolthoff adds enough sulphuric acid to correspond to a normality of 1.5. Under these conditions the titration may be performed very rapidly and the accuracy is as high as 0.1 per cent. The operations must be carried out at room temperature to prevent the decomposition of the ferrocyanide to hydrocyanic acid.

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[11] W. S. Hendrixson and L. M. Verbeck, J. Ind. Eng. Chem., **14**, 1152 (1922). *Cf.* also W. S. Hendrixson, J. Am. Chem. Soc., **47**, 1319 (1925).

[12] I. M. Kolthoff, Pharm. Weekblad, **61**, 841 (1924).

[13] Carlos del Fresno, Z. Elektrochem., **31**, 199 (1925). *Cf.* also S. Popoff and J. Whitman, J. Am. Chem. Soc., **47**, 2259 (1925).

[14] G. L. Kelley and R. T. Bohn, J. Am. Chem. Soc., **41**, 1776 (1919).

Erich Müller and H. Lauterbach [16] have confirmed Kolthoff's results; they titrate to an inflection-potential of 0.66 volt (against N.C.E.). They perform the titration in very dilute solution.

According to Kelley and Bohn, large quantities of hydrochloric acid interfere. Kolthoff, using a bright electrode, did not confirm this finding, although he noticed that the break in potential at the end-point is less sharp. Reaction between the permanganate and hydrochloric acid occurs when an excess of permanganate is present. The addition of hydrochloric instead of sulphuric acid is advantageous because the former acid prevents the precipitation of the interfering manganous salt much more completely than does sulphuric acid. The precipitation of the manganous salt was prevented by having the concentration 0.8 N with respect to hydrochloric acid when the normality of ferrocyanide was 0.025. The hydrochloric acid has an interfering action in very dilute ferrocyanide solutions (0.002 N).

The ferrocyanide titration with permanganate may be

[15] I. M. Kolthoff, Rec. trav. chim., **41**, 343 (1922).

[16] Erich Müller and H. Lauterbach, Z. analyt. Chem., **61**, 398 (1922).

applied in the determination of zinc (Kolthoff and Verzijl,[17] *cf.* p. 268). Fifty cubic centimeters of water are added to 10 cc. of 0.1 N zinc solution, and 50 cc. 0.1 N(= 1/40 molar) potassium ferrocyanide, and then 25 cc. 4 N sulphuric acid. The excess of ferrocyanide is determined with permanganate, without first removing the precipitate. The potential break is very sharp because of the extreme insolubility of the zinc-potassium ferrocyanide, and it occurs exactly at the equivalence-point. If the excess of ferrocyanide is determined according to the ordinary titration method the color change at the end-point is rather vague.

*Titration of Ferrous Iron:*

$$MnO_4^- + 5Fe^{++} + 8H^+ \rightleftarrows Mn^{++} + 4H_2O + 5Fe^{+++}.$$

Partial reactions:

$$MnO_4^- + 8H^+ + 5\ominus \rightleftarrows Mn^{++} + 4H_2O;$$

$$\varepsilon_0 = 1.217 \text{ volt (N.C.E.)}$$

$$5Fe^{++} \rightleftarrows 5Fe^{+++} + 5\ominus;$$

$$\varepsilon_0 = 0.466 \text{ volt (N.C.E.)}$$

Kelley, Adams and Wiley [18] studied this titration in connection with the potentiometric determination of chromium in steel. Kolthoff [19] did not obtain very accurate results when the electrodes were platinized (error + 0.4 per cent); with bright platinum gauze the titration is highly accurate and Mohr's salt may be used as a standard for the oxidizing power of the permanganate (Kolthoff, 1924). There is a sharp break in potential at the end-point; the potential rapidly assumes a constant value after additions of reagent. According to E. Müller and H. Möllering [20] the break occurs just before the pink color of the permanganate is visible; the results are accurate. They found the inflection-potential at 0.65 (against N.C.E.), in 0.4 N sulphuric acid. This inflection-potential of course varies with the acid concentration of the solution. The reverse titration of permanganate with ferrous sulphate is not practicable, as manganese dioxide is formed during the titration and reacts slowly with ferrous ion. Hence the titration must be made quickly. Inflection-potential + 0.76 volt.

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[17] E. J. A. Verzijl, De Potentiometrische Zinktitratie, Diss. Utrecht (1923).

[18] Kelley, Adams and Wiley, J. Ind. Eng. Chem., **9**, 780 (1917).

[19] I. M. Kolthoff, Chem. Weekblad, **16**, 450 (1919).

[20] E. Müller and H. Möllering, Z. anorg. Chem., **141**, 111 (1924).

Müller and Möllering (*loc. cit.*) found an inflection-potential of + 0.67 volt (in 0.4 N HCl) in the titration of ferrous salt in the presence of hydrochloric acid. They found the titration to be as accurate in this medium as in sulphuric acid solution. The authors can not confirm this result; because of chlorine formation, the break occurs too late. Addition of manganous salt improves the result.

*Uranium*:

$$2MnO_4^- + 5U^{++++} + 2H_2O \rightleftarrows 2Mn^{++} + 5UO_2^{++} + 4H^+.$$

With the partial reactions:

$$2MnO_4^- + 16H^+ + 10\ominus \rightleftarrows 2Mn^{++} + 8H_2O;$$

$$\varepsilon_0 = 1.217 \text{ volt (against N.C.E.)}$$

$$5U^{++++} + 10H_2O \rightleftarrows 5UO_2^{++} + 20H^+ + 10\ominus;$$

$$\varepsilon_0 = 0.100 \text{ volt (against N.C.E.)}$$

As may be seen from the equations, the reduction potential of an uranous solution is also dependent upon the hydrogen-ion concentration:

$$U^{++++} + 2H_2O \rightleftarrows UO_2^{++} + 4H^+ + 2\ominus,$$

$$E = \varepsilon_0 + \frac{0.059}{2}\log\frac{[UO_2^{++}][H^+]^4}{[U^{++++}]}.$$

Luther and Michie[21] found the following values for the potential of an uranous-uranyl solution at different hydrogen-ion concentrations:

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[21] Luther and Michie, Z. Elektrochem., **24**, 826 (1908); Evans, J. Am. Chem. Soc., **31**, 371 (1909); McCoy and Bunzel, *ibid.*, **31**, 367 (1909).

| | $\frac{[UO_2^{++}]}{[U^{++++}]} = 10^{-3}$ | | | $\frac{[UO_2^{++}]}{[U^{++++}]} = 10^{3}$ | | |
|---|---|---|---|---|---|---|
| $[H^+]$ | 0.0611 | 0.278 | 0.538 | 0.0611 | 0.278 | 0.538 |
| E | 0.194 | 0.271 | 0.304 | 0.368 | 0.445 | 0.478 |

*Titration.*—D. T. Ewing and E. F. Eldredge [22] mix 10 cc. of uranium solution with 40 cc. of approx. 2 per cent sulphuric acid and warm to 80–90°. The air is removed with carbon dioxide. The solution is slowly passed through a Jones reductor which is finally rinsed with 50 cc. of 2 per cent sulphuric acid. The reduced solution is brownish because of the presence of trivalent uranium. There are two jumps in potential in the titration with potassium permanganate: the first when $U^{III}$ is oxidized to $U^{IV}$ (the solution then becomes greenish), and the second when all $U^{IV}$ is oxidized to $UO_2^{++}$. From the amount of reagent used between the first and second breaks ($U^{IV} \rightarrow UO_2^{++}$) the uranium content may be calculated. Ewing and Eldredge found no sharp break at the end of the oxidation of $U^{IV}$ when the solution contained more than 2 per cent of sulphuric acid. The titration must be carried out in an atmosphere of carbon dioxide.

R. G. Gustavson and C. M. Knudson [23] were unable to confirm the results of Ewing and Eldredge. After reduction they found all of the uranium in the quadrivalent form; according to their findings the titration is accurate in strongly acid solution (30 per cent sulphuric acid).

E. Müller and A. Flath [24] failed to find trivalent uranium after reduction with zinc, thus confirming the results of Gustavson and Knudson. The authors would suggest that the degree of acidity during the reduction will have an influence upon the intensity of the reduction. A point of difference was that Gustavson and Knudson did not titrate in a carbon dioxide atmosphere.

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[22] D. T. Ewing and E. F. Eldredge, J. Am. Chem. Soc., **44**, 1484 (1922).

[23] R. G. Gustavson and C. M. Knudson, J. Am. Chem. Soc., **44**, 2756 (1922).

[24] E. Müller and A. Flath, Z. Elektrochem., **29**, 500 (1923).

W. D. Treadwell[25] performed the reduction by slowly pouring the solution through a cadmium reductor, and collecting it in a vessel from which the air had not been removed. If the air is removed with carbon dioxide too much reagent is used. Hence Treadwell makes use of the statement of McCoy and Bunzel (*loc. cit.*) that trivalent uranium is readily oxidized in air to the quadrivalent form. The final titration of $U^{IV}$ to $UO_2^{++}$ with permanganate is made in a stream of carbon dioxide. Treadwell recommends that the solution be warm when titrated as more regular results are obtained than in the cold. This has been confirmed by Müller and Flath (*loc. cit.*)

*Uranium and Iron.*—Ewing and Eldredge (*loc. cit.*) titrated the reduced solution with permanganate (or dichromate). There is a jump in potential after the oxidation of $U^{IV}$ to $UO_2^{++}$; the iron is then oxidized, after which a second jump occurs. Gustavson and Knudson (*loc. cit.*) and Müller and Flath (*loc. cit.*) found that the results were accurate, if the acidity was kept low after the reduction. Optimum concentration: 5 cc. conc. sulphuric acid per 250 cc. of solution.

*Vanadium.*—According to Gustavson and Knudson (*loc. cit.*) vanadic acid is reduced by zinc in sulphuric acid solution to a salt of the oxide $V_2O_2$. In the permanganate titration this is first oxidized to $V_2O_3$, then to $V_2O_4$, and finally to $V_2O_5$. We therefore find three potential breaks in the titration of the reduced solution, corresponding to the formation of these three different oxidation products. A high acidity was found to favor sharp inflections at the different end-points. According to Treadwell (*loc. cit.*) the reduction to $V^{II}$ may be accomplished by the cadmium reductor. E. Müller and A. Flath (*loc. cit.*) found sharper maxima when the titration was made at 80°.

*Vanadium and Iron.*—In the presence of iron three breaks in potential again occur; the volume of permanganate represented by the distance between the first and second inflections includes both the quantity used to oxidize the iron and that which is necessary to oxidize vanadium from the trivalent to the quadrivalent condition. If the amount of permanganate used for the oxidation of $V^{III}$ to $V^{IV}$ – which is equivalent to the difference between the second and third inflections—is subtracted from the amount used between the first and second inflections, we have the volume used in the oxidation of the iron. The titration must be carried out in an indifferent atmosphere.

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[25] W. D. Treadwell, Helv. Chim. Acta, **5**, 732,806 (1922); *cf.* also *ibid.*, **2**, 696 (1919).

Müller and Flath (*loc. cit.*) did not confirm the results of Gustavson and Knudson in all particulars. When iron is present the end of the oxidation $Fe^{II}$ to $Fe^{III}$ is indicated very sharply in the potential curve, but not that of $V^{III}$ to $V^{IV}$. When titrating at 80° the break after the latter oxidation is very sharp, but that after the complete oxidation of iron is very vague. Müller and Flath recommend that the solution be at 80° until the second jump in potential is reached; the liquid is then cooled and the iron is oxidized at room temperature.

*Vanadium and Uranium.*—Gustavson and Knudson found in this instance, as in the case of iron and vanadium, that the volume between the first two inflections includes all of the uranium and one of the vanadium oxides. Therefore upon subtracting the volume used between the last two inflections, we have the amount of permanganate used in the titration of uranium. Müller and Flath only found good results when the titration was made at 80°.

*Vanadium, Uranium, and Iron.*—The degree of acidity is of great importance in this case. Gustavson and Knudson add 4 cc. of conc. sulphuric acid to 250 cc. of the solution; after the second inflection has been found an additional 4 cc. of the acid is added and the titration continued. The volume of reagent required between the third and final inflections represents one step in the oxidation of vanadium; that between the second and third inflection represents iron; whereas the volume between the first and second inflections is the sum of the permanganate necessary to oxidize all of the uranium and that required for the oxidation of the vanadium from the trivalent to the quadrivalent condition. Since the amount of permanganate necessary to oxidize vanadium trioxide to the tetroxide is the same as that required for the oxidation of the tetroxide to the pentoxide, we can find the volume of reagent corresponding to the uranium by subtracting the volume representing the latter oxidation from the volume used between the first and second inflections. It is thus possible to calculate the quantities of vanadium, uranium, and iron from the data of a single titration. Müller and Flath again recommend titration at 80° until the second sharp rise in potential, then at room temperature until the iron is oxidized, and finally at 80° until the last inflection is found.

When the solution contains vanadium in the presence of a very large amount of iron, it is best to reduce the vanadic acid to the vanadyl condition with ferrous sulphate.[26] The latter can be oxidized to vanadic acid by permanganate; best results are obtained at 70°–80°. An accurate vanadium determination is possible, even when chromic salts are present.[27] Müller and Just add 50 g. of sulphuric acid per liter of solution and titrate at 70° until an inflection-potential of 0.91 volt (against N.C.E.) is reached.

*Niobium.*—The hydrochloric acid solution of the metal is poured through the cadmium reductor five times. According to Treadwell[28] the niobium is then in the trivalent state and may be oxidized with permanganate or with ferric chloride.

*Molybdic Acid* in hydrochloric acid solution is reduced by lead and may then be titrated with permanganate after the addition of manganous salt. According to Treadwell accurate results are obtained when air is excluded.

*Stannic* solutions are also reduced by lead, and the stannous tin may be oxidized with permanganate (Treadwell).

*Titanic* solutions are reduced to the titanous state in the cadmium reductor (Treadwell). The reduced solution may be titrated with permanganate or dichromate. In the presence of iron two inflections are observed; the first corresponding to the completion of the oxidation, $Ti^{III}$ to $Ti^{IV}$, and the second to $Fe^{II} \rightarrow Fe^{III}$. (*Cf.* p. 291 on the standardization of titanous solutions.) Treadwell used a platinized electrode upon finding that smooth electrodes did not give reproducible values. Kolthoff could not confirm this, and prefers bright platinum electrodes because the platinized ones catalyze the oxidation of the titanous solution.

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[26] G. L. Kelley and J. B. Conant, J. Am. Chem. Soc., **38**, 341 (1916); H. H. Willard and F. Fenwick, J. Am. Chem. Soc., **45**, 84 (1923).

[27] E. Müller and H. Just, Z. anorg. Chem., **125**, 155 (1922). I. M. Kolthoff and O. Tomicek, Rec. trav. chim., **43**, 447 (1924).

[28] W. D. Treadwell, Helv. Chim. Acta, **5**, 732,806 (1922).

*Indigo, Thioindigo, and Methylene Blue* are reduced by the cadmium reductor (W. D. Treadwell) and may afterwards be titrated with permanganate, ferric chloride, or other oxidants. Care should be taken to exclude air.

*Manganous Salts* may be titrated potentiometrically according to the Volhard-Wolff method. E. Müller and O. Wahle[29] have published several papers which deal with the application of this method. The reaction is represented by the equation:

$$2MnO_4^- + 3Mn^{++} + 2H_2O \rightleftarrows 5MnO_2 + 4H^+.$$

The results are good only when the permanganate is added to the warm (80°–90°) solution, which must contain a sufficient amount of zinc sulphate, potassium nitrate, or other electrolyte. The results are in agreement with the usual Volhard method.

A greater break is obtained when the titration is carried out in the presence of hydrofluoric acid. In this case the course of the reaction is:

$$MnO_4^- + 4Mn^{++} + 8H^+ \rightleftarrows 5Mn^{+++} + 4H_2O.$$

Ten cc. of 4N sulphuric acid are added to 100 cc. of the solution, which must contain 8 g. of potassium fluoride. The titration is made with the solution at 80° (platinum dish). The stirrer is of hard rubber and the end of the salt bridge, which dips into the solution, is a hard rubber tube.

For the determination of manganese in presence of iron it is best to oxidize the iron with bichromate. If the oxidation is made with permanganate an excess of manganous ions is brought into the solution, for which a correction must later be applied. Hence Müller and Wahle (*loc. cit.*) titrate the iron with potassium dichromate in acid solution until an inflection-potential of + 0.575 volt (against N.C.E.) is reached. The solution, which does not contain an excess of dichromate, is run into a platinum dish and treated with fluoride. The manganese is then titrated as described above.

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[29] E. Müller and O. Wahle, Z. anorg. Chem., **129**, 33,278 (1923); **130**, 63 (1923); **132**, 260 (1923).

**2. Potassium Dichromate.**—The oxidizing action of dichromate may be represented by the equation:

$$Cr_2O_7^{=} + 14H^+ + 6 \ominus \rightleftarrows 2Cr^{+++} + 7H_2O,$$

and the potential relations by:

$$E = \varepsilon_0 + \frac{0.059}{6} \log \frac{[Cr_2O_7^{=}][H^+]^{14}}{[Cr^{+++}]^2}.$$

When we keep the ratio $[Cr_2O_7^{=}] : [Cr^{+++}]^2$ constant, the electrode should change $14 \cdot \frac{0.059}{6} = 0.135$ volt for each variation of 1 in $p_H$.

The actual behavior of the dichromate electrode differs from that which we should expect from theoretical considerations. This conclusion follows from the experiments of Luther[30] and of Kolthoff.[31] By way of illustration, some of the values which Luther[30] found are given in the following table. He diluted his

MEASUREMENTS OF LUTHER

| Electrolyte Added | Approximate Value of $p_H$ | E.M.F. against Ag*n*AgCl Electrode | Δ in E.M.F. per 1 in $p_H$ |
|---|---|---|---|
| +1 vol. 2 N HCl.......... | 0 | 1.56 | 0.24 |
| +1 vol. 0.2 N HCl.......... | 1 | 1.32 | 0.14 |
| +1 vol. 0.02 N HCl.......... | 2 | 1.18 | 0.05 |
| +1 vol. acetate mixture....... | 3 | 1.13 | 0.05 |
| +1 vol. acetate mixture....... | 4 | 1.08 | 0.06 |
| +1 vol. acetate mixture....... | 5 | 1.02 | 0.09 |
| +1 vol. acetate mixture....... | 6 | 0.93 | |

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[30] R. Luther, Z. physik. Chem., **30**, 653 (1899).

[31] I. M. Kolthoff, Chem. Weekblad, **16**, 450 (1919).

standard mixture, which consisted of 0.2 N potassium chromate and 0.1 N chromic sulphate, with one volume of the electrolyte. the measurements were made against the 0.1 N silver-silver chloride electrode.

Luther remarks that the measurement is attended with many difficulties, as Kolthoff also found. The latter found that it makes a considerable difference whether the solution is acidified with sulphuric or hydrochloric acid. Some of his recent measurements (unpublished) are given in the following table. The potassium dichromate was 0.01 N (1/300 molar), and the solutions were of different $p_H$. The electrode was a bright platinum gauze. Measurements were at 25° against N.C.E.

MEASUREMENTS OF KOLTHOFF

| Concentration of Added Electrolyte | Approximate $p_H$ | E.M.F Against N.C.E. at 25° C. |
|---|---|---|
| | 4.5 | 0.428 |
| Biphthalate — Hydrochloric Acid Buffer... | 3 | 0.492 |
| 0.011 N sulphuric acid.................. | 2 | 0.578 |
| 0.125 N sulphuric acid.................. | 1 | 0.655 |
| 2 N sulphuric acid.................. | 0 | 0.785 |
| 0.01 N hydrochloric acid................ | 2 | 0.580 |
| 0.1 N hydrochloric acid................ | 1 | 0.600 |
| 1 N hydrochloric acid................ | 0 | 0.691 |
| 1 N hydrochloric acid, $CrCl_3$......... | 0 | 0.689 |

From these tables we see that there is no regular relation between $p_H$ and the oxidation potential of dichromate. Moreover, the effect of trivalent chromium is very peculiar. Sometimes the potential increases with increasing amount of chromic ion, instead of the electrode becoming less noble as we should expect. This may be an explanation of the peculiar shape of the titration curve of dichromate and ferrous iron.[32] As the behavior of the dichromate electrode has not yet been explained from a theoretical point of view, it is not possible to make exact calculations of the value of the equivalence-potential when dichromate is the oxidant. It is, however, a very suitable reagent in the titration of various reductants as it is a strong and rapidly acting oxidant. In most cases, the reduced form of metals, etc., which may be titrated with permanganate (*cf.* § 1), e.g., ferrous iron, uranous salts, etc., may also be titrated with dichromate.

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[32] *Cf.* for example, Forbes and Bartlett, J. Am. Chem. Soc., **35**, 1535 (1913).

The potassium dichromate may readily be obtained in a pure condition by recrystallizations from water and drying at 200°, or better, melting in an electric oven.

*Titration of Ferrous Iron*:

$$Cr_2O_7^{=} + 14H^+ + 6Fe^{++} \rightleftarrows 2Cr^{+++} + 7H_2O + 6Fe^{+++}.$$

With partial reactions:

$$Cr_2O_7^{=} + 14H^+ + 6\ominus \rightleftarrows 2Cr^{+++} + 7H_2O,$$

$$6Fe^{++} \rightleftarrows 6Fe^{+++} + 6\ominus.$$

In his classical paper, J. H. Hildebrand [33] made a study of the potentiometric titration of ferrous iron with bichromate. Neither he nor G. S. Forbes and E. P. Bartlett [34] discuss the accuracy of the titration. Kolthoff [35] showed that the acidity was of importance; sulphuric acid as well as hydrochloric acid may be used. In agreement with Kolthoff, M. Eppley and W. C. Vosburgh [36] showed that constant results are obtained in solutions of which the acid concentration is between 0.4 and 2.5 N hydrochloric, or above 0.4 N sulphuric (*cf.* Hildebrand, *loc. cit.*)

Dissolved air has a negligible effect on the titration. The results are somewhat dependent on the dilution of the solution. In the titration of 0.01 N ferrous solution, the amount of dichromate required is about 0.4 per cent higher than the calculated amount; the deviation increases slowly in more dilute solutions. Hydrofluoric and phosphoric acids have almost no influence on the result. W. D. Treadwell and L. Weiss [37] found that a warm solution acidified with sulphuric acid could be titrated with an accuracy of about 0.5 per cent. In the authors' opinion, a further systematic study of the factors which influence the accuracy of the ferrous iron-dichromate titration would be very desirable.

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[33] J. H. Hildebrand, J. Am. Chem. Soc., **35**, 847 (1913).

[34] G. S. Forbes and E. P. Bartlett, J. Am. Chem. Soc., **35**, 1535 (1913).

[35] I. M. Kolthoff, Chem. Weekblad, **16**, 450 (1919).

[36] M. Eppley and W. C. Vosburgh, J. Am. Chem. Soc., **44**, 2140 (1922).

[37] W. D. Treadwell and L. Weiss, Helv. Chim. Acta, **2**, 695 (1919).

J. C. Hostetter and H. S. Roberts[38] have applied the potentiometric method to the determination of traces of iron in commercial salts. The titration is carried out in an atmopshere of indifferent gas; the accuracy is about 1 per cent.

The method has also been applied to the determination of iron in optical glasses,[39] and of iron in magnetite.[40]

The reverse titration—dichromate with ferrous iron—has been applied by G. L. Kelley and J. B. Conant[41] for the determination of chromium in steel. According to Eppley and Vosburgh (*loc. cit.*) the results of this titration agree with the titration of ferrous iron with dichromate.

*Titration of Trivalent Antimony.*—M. H. Fleysher[42] oxidizes the trivalent antimony with dichromate. The rise in potential at the end-point is only 80–100 millivolts.

*Stannous Salts.*—According to Fleysher the jump in potential at the end-point is very large (*cf.* also Hostetter and Roberts (1919), and H. R. Adam (1924)). Fleysher does not mention the course of the potential in the titration of a mixture of stannous and antimonious solutions. Stannous tin is first oxidized, after which there is a sharp potential change; the oxidation of antimony to the quinquivalent state then follows. Instead of making this simple titration, Fleysher removes the stannous ion by adding mercuric chloride and titrates the antimony without previous filtration. He remarks that arsenious solutions may be titrated in a similar way. In the authors' opinion this mode of titration gives rise to many difficulties.

*Iodide.*—I. M. Kolthoff[43] studied the titration of iodide with dichromate. The break is very small when the solution is acidified with sulphuric acid. When hydrochloric acid is used, far better results are obtained. In about 1 N HCl solution the results are accurate to 0 to 0.4 per cent. Bromides decrease the jump in potential, but it is still possible to titrate with an accuracy of 1 per cent when the ratio $I^- : Br^-$ is larger than 1 : 5.

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[38] J. C. Hostetter and H. S. Roberts, J. Am. Chem. Soc., **41**, 1337 (1919).

[39] J. B. Ferguson and J. C. Hostetter, J. Am. Ceramic Soc., **2**, 608 (1919).

[40] H. R. Adam, J. S. African Chem. Inst., **8**, 7 (1925).

[41] G. L. Kelley and J. B. Conant, J. Ind. Eng. Chem., **8**, 719 (1916); *cf.* also *ibid.*, **9**, 780 (1917); **13**, 1053 (1921).

[42] M. H. Fleysher, J. Am. Chem. Soc., **46**, 2725 (1924).

[43] I. M. Kolthoff, Rec. trav. chim., **39**, 208 (1920).

W. S. Hendrixson[44] says: "Apparently hydriodic acid can be titrated directly against neither dichromate nor iodate by running their solutions into hydriodic acid to the end-point. There is no such abrupt rise in potential as in the case of permanganate, and the position of the end-point is not so evident." In a later paper Hendrixson[45] states that the direct titration with dichromate is possible in sulphuric acid solution of at least 2 N concentration, if sufficient time is allowed near the end-point for the reaction to reach completion. At least half an hour is required to reach the end-point without overstepping. Hendrixson did not use hydrochloric instead of sulphuric acid.

**3. Oxidation with Potassium Iodate.**—The oxidizing action of iodate ion may be represented by the equation:

$$IO_3^- + 6H^+ + 6\ominus \rightleftarrows I^- + 3H_2O.$$

Potassium iodate may be obtained in pure condition by recrystallization from water and drying at 180°.

*Iodide.*—According to I. M. Kolthoff,[46] the potentiometric titration of iodide with iodate yields very accurate results. The reaction is represented by the equation:

$$IO_3^- + 5I^- + 6H^+ \rightleftarrows 3H_2O + 3I_2.$$

With partial reactions:

$$IO_3^- + 6H^+ + 5\ominus \rightleftarrows \tfrac{1}{2}I_2 + 3H_2O$$

$$5I^- \rightleftarrows 2\tfrac{1}{2}I_2 + 5\ominus.$$

The solution may be acidified with hydrochloric or sulphuric acid. The potential becomes steady very soon and a sharp break occurs at the equivalence-point. Accuracy, 0.1 per cent. Presence of bromide decreases the accuracy and the magnitude of the potential break, but good results are obtained when the ratio I : Br is larger than 1 : 5.

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[44] W. S. Hendrixson, J. Am. Chem. Soc., **43**, 19 (1921).

[45] W. S. Hendrixson, J. Am. Chem. Soc., **43**, 1313 (1921).

[46] I. M. Kolthoff, Rec. trav. chim., **39**, 212 (1920).

W. S. Hendrixson[47] studied the titration of iodate with iodide. He found it impracticable in hydrochloric acid solution because of reaction between acid and iodate (volatilization of chlorine?). With sulphuric acid he found a sharp end-point although the reaction at the end-point is slower than in the titration of iodide with permanganate.

Recently E. Müller and D. Junck[48] have studied the iodide-iodate reaction. They recommend that the solution be acidified with sulphuric acid. With the use of hydrochloric acid the break decreases with increasing acid concentration because of the formation of iodine chloride:

$$2I^- + IO_3^- + 6H^+ + 3Cl^- \rightleftarrows 3ICl + 3H_2O.$$

When this reaction is complete a second jump in potential occurs even in solutions with a hydrochloric acid concentration as small as 0.4 N. Kolthoff was unable to confirm this statement, and he did not find a pronounced maximum at the point where ICl is formed quantitatively, even at higher acid concentrations. With the use of sulphuric acid, Müller and Junck found an inflection-potential of + 0.652 against the N.C.E.[49]

*Sulphite.*—W. S. Hendrixson[50] studied the oxidation of sulphurous acid with bromate, dichromate, and iodate. The amounts of bromate and dichromate are less than those required by theory for the complete oxidation to sulphate, to about the same extent as the results for permanganate. The discrepancy is attributed to the same cause, the formation of dithionic acid which resists further oxidation. On the other hand, iodate oxidizes sulphite completely to sulphate. It is recommended that the sulphite solution be added to that of the iodate. Two

[47] W. S. Hendrixson, J. Am. Chem. Soc., **43**, 861 (1921).

[48] E. Müller and D. Junck, Z. Elektrochem., **31**, 200 (1925).

[49] On p. 205 of their paper, Müller and Junck recommend an inflection-potential of + 0.580 volt.

[50] W. S. Hendrixson, J. Am. Chem. Soc., **47**, 1319 (1925).

sharp breaks in potential occur at the completion of the equations:

$$2IO_3^- + 5SO_3^= + 2H^+ \rightleftarrows I_2 + 5SO_4^= + H_2O \quad \text{(1st break)},$$

and

$$I_2 + SO_3^= + H_2O \rightleftarrows 2H^+ + 2I^- + SO_4^= \quad \text{(2nd break)}.$$

The results were accurate when the iodate was 1 to 3 N with respect to sulphuric acid.

*Thiocyanate.*—F. Fenwick [51] applied the Andrew method for the oxidation of thiocyanate with iodate.[52] The reaction is:

$$4CNS^- + 6IO_3^- + 6Cl^- + 8H^+ \rightleftarrows 4SO_4^= + 6ICl + 4HCN + 2H_2O.$$

Miss Fenwick used the polarized bimetallic system. She states: " In a solution containing not less than 10 per cent by volume of conc. hydrochloric acid, to prevent the hydrolysis of iodine monochloride, the electrometric end-point in titrations with iodate is very sharp." . . . " The initial potential is low, beginning to rise slightly about 0.4 cc. before the completion of the reaction. The final break is very sharp, about 250 millivolts during the addition of 0.02–0.03 cc. of the titrating solution. There is no further appreciable rise or fall; the usual fall with excess of oxidizing agent is absent." . . . " The titration may be carried out more rapidly and accurately than with the usual chloroform indicator." Probably the ordinary potentiometric system will also give accurate results.

**4. Oxidation with Potassium Bromate.**—The oxidizing action of bromate may be represented by the equation: [53]

$$BrO_3^- + 6H^+ + 6\ominus \rightleftarrows Br^- + 3H_2O.$$

Potassium bromate may be obtained in pure state by recrystallization from water and drying at 180°.

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[51] F. Fenwick, Dissertation, Ann Arbor (1922), p. 76.

[52] Andrew, J. Am. Chem. Soc., **25**, 756 (1903); Jamieson, Levy and Wells, J. Am. Chem. Soc., **30**, 760 (1908).

[53] *Cf.* Luther and Sammet, Z. physik. Chem., **53**, 641 (1905).

*Ferrous Iron:*

$$BrO_3^- + 6H^+ + 6Fe^{++} \rightleftarrows Br^- + 3H_2O + 6Fe^{+++}.$$

I. M. Kolthoff [54] used the potentiometric method for the titration of ferrous iron with bromate. When the solution was acidified with hydrochloric acid a sharper break was obtained at the end-point than with the use of sulphuric acid. Although the odor of bromine is noticeable during the titration, the results are accurate to about 0.3 to 0.5 per cent. Phosphoric acid makes the inflection vague and should not therefore be used.

According to F. Fenwick (*loc. cit.*) the oxidation of ferrous iron by bromate is slow, but in the presence of a small amount of a cupric salt the velocity of the reaction is increased to such an extent that an excellent end-point is obtained. A high concentration of hydrochloric acid is necessary; about 15–20 per cent gives ideal results; the end-point is very sensitive. The magnitude of the break (bimetallic system) is not great—about 30 to 40 millivolts—but the drop in potential with excess of reagent is more than usually distinct because of the formation of free bromine.

*Cuprous Copper:*

$$BrO_3^- + 6H^+ + 6Cu^+ \rightleftarrows Br^- + 3H_2O + 6Cu^{++}.$$

E. Zintl and H. Wattenberg [55] reduce the cupric solution with an excess of titanous chloride solution and titrate back with potassium dichromate or bromate. The excess of titanous salt is first oxidized:

$$BrO_3^- + 6H^+ + 6Ti^{+++} \rightleftarrows Br^- + 3H_2O + 6Ti^{++++},$$

and then the cuprous salt.

The amount of reagent required between the first and second jumps in potential corresponds to the copper content. The best results are obtained when the solution contains 4 to 8 per cent of hydrochloric acid and the titration is made at 80°. Air is removed by the passage of a stream of carbon dioxide. When the bromate or dichromate is not prepared in air-free water a correction is applied because 0.25 per cent too little reagent is used. (The correction will be dependent upon the dilution of the solution.) Ammonium salts have an interfering action; iron is titrated with the copper. When the titanous solution contains iron, as is usually the case, a correction has to be applied for the iron (*cf.* application of titanous salts, p. 292). Nitric acid also has a disturbing influence unless enough reagent is added to reduce it completely. Even in this case it requires a long time for the potential to become constant.

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[54] I. M. Kolthoff, Chem. Weekblad, **16**, 457 (1919).

[55] E. Zintl and H. Wattenberg, Ber., **35**, 3366 (1922).

*Arsenic and Antimony:*

$$BrO_3^- + 6H^+ + 3As^{+++} \rightleftarrows Br^- + 3H_2O + 3As^{\overset{++}{+++}}.$$

According to Zintl and Wattenberg,[56] trivalent arsenic and antimony behave in the same way, and may be titrated with bromate at room temperature when the solution contains at least 5 per cent of hydrochloric acid. Inflection-potential in both cases, + 0.78 volt (against N.C.E.).

The method is very suitable for the determination of antimony in the presence of arsenic. The sum of the two elements is determined by bromate titration. Quinquivalent arsenic is only reduced with great difficulty, while the antimony is completely reduced to the trivalent state by an excess of titanous chloride. The solution of the quinquivalent antimony, which must contain at least 5 per cent of hydrochloric acid, is heated to boiling, and titanous chloride is run in until the potential of the bare platinum electrode is 0.3 volt (against N.C.E.). A few drops of 3 per cent copper sulphate are then added and the liquid is stirred in the presence of air until the potential has increased to 0.5 volt. At this point the excess of titanous solution has been oxidized; the process is accelerated by the presence of the copper salt. The antimony, now entirely in the trivalent state, is titrated with bromate. Under the conditions above described, arsenic is not reduced by the small excess of titanous chloride, if the excess is removed soon (*cf.*

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[56] E. Zintl and H. Wattenberg, Ber., **56**, 472 (1923).

p. 294). Hence we may determine antimony in the presence of arsenic by this simple process.

*Iodide.*—Hydriodic acid may be titrated directly with bromate solution in the presence of hydrochloric or sulphuric acid. In the former case, Kolthoff[57] obtained the best results when the solution was 0.7 N with respect to HCl. The theoretical results were obtained. A disadvantage is that it takes a long time for the potential to become constant near the equivalence-point. The break is much smaller when bromide is present; yet Kolthoff obtained results which did not differ more than 0.2 per cent from the theoretical value when the ratio I : Br was not larger than 1 : 5. W. S. Hendrixson[58] titrated in the presence of at least 2 N sulphuric acid. The last drops of bromate solution must be added very slowly in order to avoid running past the end-point. According to Hendrixson the titration requires at least fifteen minutes merely to obtain the correct end-point, and much longer to construct the titration curve. The results are very concordant. He found a good potential break in hydrochloric acid solution, but it appeared too late (error, 1.2–2.5 per cent). He therefore recommends the use of sulphuric acid.

**5. Titration with Other Oxidants.**—*Use of Hypochlorite in Determination of Sulphite.*—Hypochlorite oxidizes sulphite to sulphate:

$$ClO^- + SO_3^= \rightleftarrows Cl^- + SO_4^=.$$

Bechler[59] has applied this reaction potentiometrically. The magnitude of the break decreases with increasing alkalinity. A good end-point is obtained in a suspension of magnesium hydroxide and the method may therefore be used for the determination of sulphur dioxide in gases that contain carbon dioxide. Inflection-potential, + 0.32 volt (against N.C.E.). In the authors' opinion there is danger of volatilization of hypochlorous acid when the gas which is to be tested is passed through the solution.

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[57] I. M. Kolthoff, Rec. trav. chim., **39**, 211 (1920).

[58] W. S. Hendrixson, J. Am. Chem. Soc., **43**, 1311 (1921).

[59] Bechler, Dissertation, Dresden (1922); *cf.* E. Müller, Die Elektrometrische Massanalyse, 2d Ed., p. 141.

*The Application of the Potentiometric Method in the Technical Preparation of Hypochlorite.*—E. Müller[60] has made a very promising application of the potentiometric method in the technical preparation of solutions of calcium hypochlorite and sodium hypochlorite. The latter solution has distinct advantages over the calcium salt solution, because the calcium salt may be taken up by cotton which is being bleached and later cause stains.

When chlorine is passed into a sodium hydroxide solution, a solution of high sodium hypochlorite content is obtained. The solution is most efficient in action when equivalent amounts of alkali and hypochlorous acid are present. When such a solution bleaches fabric no acid is formed; on the other hand, the solution is not so alkaline as to give a rapid decomposition into chlorate. We can not use an indicator in the preparation of such an " equivalent " hypochlorite solution because the indicator is destroyed by the oxidant. The potential of an unattackable electrode, however, serves as an indicator. The potential of a hypochlorite electrode is dependent upon the hydrogen-ion concentration of the liquid:

$$ClO^- + 2H^+ + 2\ominus \rightleftarrows Cl^- + H_2O,$$

and

$$E = \frac{0.0591}{2}\log\frac{[ClO^-][H^+]^2}{[Cl^-]} \quad (25°).$$

When a hypochlorite solution is prepared from sodium hydroxide and chlorine we have at the equivalence-point:

$$[ClO^-] = [Cl^-], \quad \text{and} \quad E = 0.0591 \log [H^+].$$

We see that near the equivalence-point the electrode changes its potential in the same manner with hydrogen-ion concentration as the hydrogen electrode; there will be a break in potential at the equivalence-point.

With a platinum electrode the potential is not definite before chlorine is passed into the solution; the electrode acts as an air electrode. Upon the addition of a little chlorine the more positive hypochlorite potential is established and remains almost stationary until the equivalence-point is approached, when a sharp break occurs. The potential depends upon the shape and material of the electrode; a higher potential is found with a wire than with a foil. If a platinum gauze is used the inflection-potential lies at + 0.72 volt (against N.C.E.). By titrating to this point Müller obtained the following results:

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[60] E. Müller, Z. Elektrochem., **31**, 323 (1925).

| Initial Concentration of NaOH | Final Concentration of NaOH |
|---|---|
| 2.945 N | 0.035 N |
| 2.875 N | 0.050 N |
| 2.825 N | 0.040 N |
| 9.025 N | 0.052 N |

Hence, there is still a small excess of free sodium hydroxide at the equivalence-point.

Although the Müller system, in which the inflection-potential is used, yields good results, Müller attempted to devise a simpler method for technical use. The bimetallic system was not satisfactory for this purpose, although a carbon electrode in alkaline hypochlorite solution is much more positive (about 0.5 volt) than one of platinum or palladium.

Müller prefers the use of a " retarded " electrode. When the carbon electrode and a metal (gold or platinum) electrode having a potential lower than than that of carbon are dipped into sodium hydroxide, it is possible, by wrapping the metal electrode with asbestos cord, to cause the hypochlorite that is formed to come into contact with the two electrodes at different rates. The covered, or retarded, electrode attains its values more slowly than the other. At the equivalence-point the carbon electrode has its final value, whereas the covered metal electrode has a value which corresponds to a more alkaline solution. Hence such a combination of electrodes gives zero deflection of a galvanometer when the end-point is reached.

Instead of a galvanometer, Müller uses a millivoltmeter of 372 ohms internal resistance. With zero deflection of the voltmeter he found that the alkalinity of the liquid was 0.2, 0.02, and 0.15 N. Although the method is very simple it has uncertainties, as may be seen from the changing end-concentrations of sodium hydroxide. The results are dependent upon the rate at which the chlorine is passed in, and the extent of insulation of the retarded electrode. Hence the use of the method involving inflection-potential is to be preferred, and the use of the retarded electrode is not recommended.

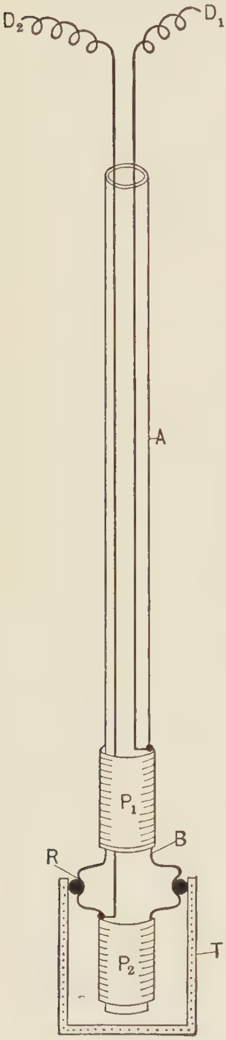

FIG. 44.—Müller immersion electrode (hypochlorite manufacture)

The most practical device consists in the use of the Pinkhof system with platinum foil as indicator electrode and a similar electrode which is placed in an " equivalent " solution of sodium hypochlorite. The latter is not easily obtained. Therefore in place of it Müller advises the use of calcium chloride mixed with milk of lime. He describes the apparatus as follows:

It consists of a glass tube, A, with a wide flattened portion, B. This portion has an indentation in its periphery, in which the tight-fitting rubber ring, R, is placed. The clay cell, T, fits snugly over the ring. (A one-hole rubber stopper may be used instead of the enlargement, B, and the rubber ring.) Two pieces of platinum foil, $P_1$, $P_2$, are fastened firmly to the glass tube above and below the enlarged portion, B, respectively. Electrical connection with these foils is made by platinum wires sealed through the glass tube, A. One end of each wire is welded to a foil ($P_1$ or $P_2$), the other to a copper lead-wire ($D_1$ or $D_2$). The interior of the tube A may be filled with paraffine, or other insulating material.

The lower foil, $P_2$, serves as a reference, the upper as an indicator electrode. The whole device is as easily manipulated as a thermometer. The clay cell, T, is filled with milk of lime and calcium chloride. If hypochlorous acid should penetrate the cell T, it would be neutralized by the lime (which is present in excess). On the other hand, any sodium hydroxide which might enter would not increase the hydroxyl-ion concentration materially because of the buffering action of the calcium chloride.

As this immersion cell gives a rather large current, a relatively insensitive millivoltmeter or galvanometer may be used. It is better, however, to use a more sensitive instrument, with suitable resistance interposed, in order to prevent polarization of the cell.

*Potentiometric Titration of Cyanide with Halogens.*—Chlorine, bromine, and iodine react with the cyanide ion to form halogen cyanide:

$$X_2 + CN^- \rightleftarrows CNX + X^-$$

where X is halogen.

If the reaction proceeds quantitatively, left to right, there will be a jump in potential when all of the halogen is transformed into halogen and cyanide. Since chlorine is the strongest oxidant the jump will be greatest in titrating with chlorine and least with iodine. According to E. Müller and A. Schuch [61] the inflection-potential in the titration with chlorine is not the same as in the reverse titration. The authors suggest that this may be due to a partial oxidation of cyanide to cyanate.

INFLECTION-POTENTIAL AGAINST NORMAL CALOMEL ELECTRODE

| Reactions | Starting With | |
|---|---|---|
| | Halogen | KCN |
| $Cl_2 + CN^- \rightleftarrows ClCN + Cl^-$ | +0.560 | +0.790 |
| $Br_2 + CN^- \rightleftarrows BrCN + Br^-$ | +0.580 | +0.580 |
| $I_2 + CN^- \rightleftarrows ICN + I^-$ | +0.210 | +0.220 |

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[61] E. Müller and A. Schuch, Z. Elektrochem., **31**, 332 (1925).

The titration is not of much importance from an analytical point of view. The potentiometric method, however, is a rapid and convenient means of preparing a solution of halogen cyanide. Müller and Schuch describe a practical arrangement for this purpose.

*Titrations with or of Iodine.*—Iodometric titrations may be carried out potentiometrically. The inflection-potential depends upon the iodide and iodine concentration of the solution. The potentiometric method is of distinct advantage in the titration of very dilute solutions. G. Oesterheld and P. Honegger [62] have applied the method to the determination of copper:

$$2Cu^{++} + 4I^{-} \rightleftarrows 2CuI + I_2$$

$$I_2 + 2S_2O_3^{=} \rightleftarrows S_4O_6^{=} + 2I^{-}.$$

C. S. Robinson and O. B. Winter [63] have studied the potentiometric titration of sulphite with iodine, in bicarbonate medium.

Details of these methods are omitted because in most practical cases the usual iodometric method will be used.

*Titration with Ferric Salts. The Potentiometric Titration of Fluorides.*—A. Gruff,[64] applied the fact that ferric ions combine with fluoride to form a complex in the titration of fluoride:

$$6F^{-} + Fe^{+++} \rightleftarrows FeF_6^{\equiv}.$$

According to W. D. Treadwell and A. Köhl [65] the method does not give reliable results. They therefore attempted to detect the end-point by the potentiometric method.

Since ferrous ion does not form a complex with fluoride, the ferrous-ferric electrode will serve for the titration of fluoride. Treadwell and Köhl used a platinized electrode; in other respects the apparatus was as described on page 150. In agreement with Gruff, they found it necessary to saturate the solution with sodium chloride in order to obtain concordant results. The use of more soluble salts like sodium perchlorate or bromide had no advantages. Potassium chloride may be used in place of the sodium salt. The greatest jumps in potential were obtained when the solution contained 50 per cent of alcohol. The addition of about 1 per cent of ferrous chloride is recommended in order to establish steady potential values at once.

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[62] G. Oesterheld and P. Honegger, Helv. Chim. Acta, **2**, 410 (1919).

[63] C. S. Robinson and O. B. Winter, J. Ind. Eng. Chem., **12**, 775 (1920).

[64] A. Gruff, Ber., **46**, 2511 (1913).

[65] W. D. Treadwell and A. Köhl, Helv. Chim. Acta, **8**, 500 (1925).

Neutral solutions are very susceptible to atmosphereic oxidation. Presumably this is due to the use of platinized platinum which is an excellent catalyst for oxidation by air. The use of a smooth platinum electrode is therefore suggested. The platinized electrode gives good results if the titration is carried out in an atmosphere of carbon dioxide. Before the titration the fluoride solution, in a platinum dish, is neutralized, phenolphthalein being used as indicator. The solution should be as concentrated as possible. The liquid is transferred to the titration flask, a minimum amount of wash-water being used. After saturation with sodium chloride, an equal volume of alcohol is added to the solution. The volume must not be greater than 100 cc. A brisk stream of carbon dioxide is now passed through the solution to remove air and to provide the requisite slight acidity.

The reagent is 0.1 N ferric chloride solution to which about 1 per cent of ferrous chloride is added. If the end-point is to be sharp the solution may not be more acid than a 0.001 N HCl solution.

The authors conclude from the data of Treadwell and Köhl that the accuracy of this titration is not very high. Even in the titration of 10 cc. of 0.1 N fluoride the uncertainty in the result seems to be of the order of 4 to 5 per cent. Treadwell and Köhl state that amounts as small as 5 mg. of fluoride may be determined with an accuracy of 0.5 mg. But this is a relative error of 10 per cent. On the other hand, it should be remarked that there are no simple methods for the titration of fluoride, and therefore if a high order of accuracy is not required the method of Treadwell and Köhl may be recommended.

*Ferric Chloride in the Determination of Tin.*—J. Pinkhof [66] obtained irregular results in titrating stannous solutions with ferric chloride, in hydrochloric acid solution. According to Kolthoff's experiments the method yields good results when the air is removed by an indifferent gas.

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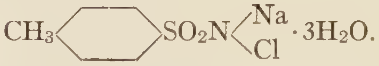
[66] J. Pinkhof, Dissertation (1919), (Amsterdam), p. 48.

*Cupric Solution in Sugar Determinations.*—W. L. Daggett, A. W. Campbell, and J. L. Whitman[67] add the reducing-sugar solution slowly to boiling Fehling's solution and read the voltage between platinum and calomel electrodes after each addition. They found a characteristic titration curve which they did not reproduce in their paper. They mix 10 cc. of copper solution (17.45 g. per liter), 10 cc. tartrate solution (with 50 g. NaOH per liter) and 50 cc. of water. This mixture requires 10.05 cc. of 1 per cent glucose solution. At the beginning of the titration the galvanometer deflection does not change rapidly, but just before the end-point a sharp break begins. These authors do not give many details.

*Chloramine T:*



This substance has been used as a disinfectant in recent years because it has a strong oxidizing action. It may be obtained in the pure state by recrystallization from water. Kolthoff (unpublished results) has employed it in the titration of iodides with highly accurate results. Ferrous iron was not readily oxidized. The authors would suggest that chloramine T may be used in the potentiometric titration of many reducing agents, especially in neutral or feebly alkaline solutions.

**6. Applications of the Ferri-ferrocyanide Electrode.**—According to the equation:

$$\text{Feoc}^{----} \rightleftarrows \text{Feic}^{---}$$

the potential of a ferri-ferrocyanide mixture will be represented by:

$$E = \varepsilon_0 + 0.059 \log \frac{[\text{Feic}]}{[\text{Feoc}]}.$$

It is evident from data in the literature, however, that the potential of the ferri-ferrocyanide electrode is also dependent upon the salt concentration, and to a very special extent upon the hydrogen-ion concentration. The latter effect may be explained by the fact that hydrogen ferrocyanide is a much weaker acid than hydrogen ferricyanide. According to Schoch and Felsing,[68] the potential depends on the concentration of potassium ion as follows:

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[67] W. L. Daggett, A. W. Campbell, and J. L. Whitman, J. Am. Chem. Soc., **45**, 1043 (1923).

$$E = \varepsilon_0 + 0.0591 \log \frac{[\text{Feic}][\text{K}^+]^x}{[\text{Feoc}]} \quad (25°)$$

where $x$ varies from 0.725 to 0.75.

According to measurements of Kolthoff [69] the potential depends upon the hydrogen-ion concentration in the following wav:

$$E = \varepsilon_0' - 0.0591 \log [\text{HCl}]^{2.22}.$$

Hence the oxidizing action increases with the acidity of the solution.

From the above it is evident that it is difficult to calculate inflection-potentials when working with the ferri-ferrocyanide electrode, because the potential is altered by the conditions under which we work.

Two kinds of applications may be made of the Feic-Feoc electrode:

*A*: Ferricyanide is used as an oxidant.

*B*: Ferrocyanide is used as a precipitant (its reducing action can not be readily applied).

*A. Oxidation with Ferricyanide.—Titration of Cerium.*—The normal potential of the system $Ce^{+++} - Ce^{++++}$ is largely dependent on the hydrogen-ion concentration of the solution. In 50 per cent potassium carbonate it is equal to + 0.063 volt; in acid medium, + 1.6 volt referred to the normal hydrogen electrode. (*Cf.* E. Bauer and A. Glaessner.[70]) Hence even the most powerful oxidizing agents are not able to oxidize trivalent cerium in acid solution. Therefore O. Tomicek [71] has made use of oxidation in alkaline medium, with ferricyanide. P. E. Browning and E. Palmer [72] had employed this method for ordinary titration, while Tomicek studied its adaptation from the potentiometric standpoint.

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[68] *Cf.* Schaum, Z. Elektrochem., **5**, 316 (1899); Schaum and v. d. Linck, Z. Elektrochem., **9**, 406 (1903); Lewis and Sargent, J. Am. Chem. Soc., **31**, 355 (1909); E. Müller, Z. physik. Chem., 88, 46 (1914); Schoch and Felsing, J. Am. Chem. Soc., **38**, 1928 (1916); Fredenhagen, Z. anorg. Chem., **29**, 398 (1902).

[69] I. M. Kolthoff, Chem. Weekblad, **16**, 1406 (1919).

[70] E. Bauer and A. Glaesner, Z. Elektrochem., **9**, 534 (1903).

The ferricyanide oxidizes the soluble potassium-trivalent cerium complex carbonates. An important fact is that none of the other rare earth or thorium salts are oxidized under these conditions, and trivalent iron is unaffected.

The following reaction takes place:

$$Fe(CN)_6^{\equiv} + Ce^{+++} \rightleftarrows Fe(CN)_6^{\overline{\equiv}} + Ce^{++++}.$$

The concentration of potassium carbonate must not be more dilute than 20 to 25 per cent at the end of the reaction; otherwise powdery precipitates are formed during the titration and the results are low.

Tomicek advises the following procedure: About three-fourths of the necessary amount of potassium ferricyanide is first added to the solution to be titrated, and carbon dioxide is passed through until all air is expelled. A strong potassium carbonate solution (about 50 per cent) is poured in, with continual stirring, until the solution contains about 30 per cent of carbonate. The titration is then completed in the usual way. The potential of the bright platinum electrode changes in a very regular way, rapidly assuming a steady value after each addition of oxidant. The inflection-potential depends on the carbonate concentration, being shifted towards more negative values as the carbonate concentration increases. In 24 per cent carbonate solution the inflection-potential is + 0.050 volt (against N.C.E.); in 48 per cent solution, + 0.030 volt; in 55 per cent solution, + 0.005 volt. The results are exact to within 0.1–0.2 per cent. Tomicek has applied the method to perocide (residue from monazite sand, containing cerium and cerite earths and sulphates) and to a pyrophoric iron alloy.

[71] O. Tomicek, Rec. trav. chim., **44**, 410 (1925).

[72] P. E. Browning and E. Palmer, Z. anorg. Chem., **59**, 71 (1908).

### TITRATION OF TITANOUS SOLUTIONS. (*Cf.* p. 298.)

*Titration of Iodide.*—The well-known iodometric titration of ferricyanide with iodide may be applied as a potentiometric titration, and according to E. Müller[73] it gives good results when the following procedure is used: an excess of zinc sulphate is added to the solution to be titrated and the ferricyanide is run in. After one to two minutes the electrode potential is constant. Inflection potential, 0.54 volt (against N.C.E.). Since the reaction is rather slow near the end-point the application of the Müller system is dangerous. The zinc sulphate is added to accelerate the reaction between ferricyanide and iodide:

$$2Fe(CN)_6^{\equiv} + 2I^- \rightleftarrows I_2 + 2Fe(CN)_6^{\underline{\equiv}}.$$

The zinc forms a double salt with the ferrocyanide, $K_2Zn_3(Feoc)_2$, which is much less soluble than zinc ferricyanide. According to Müller, the results are accurate.

The reverse titration, that of ferricyanide, mixed with zinc salt, with iodide, is impracticable.

*Titration of Hemoglobin.*—According to J. B. Conant,[74] hemaglobin is oxidized to methemoglobin by ferricyanide. The normal potential of the hemoglobin-methemoglobin electrode system depends upon the hydrogen-ion concentration. Conant gives the following table:

| $p_H$ | Referred to N $H_2$ Electrode |
|---|---|
| 6.8 | +0.092 (±0.022) |
| 8.5 | +0.115 (±0.011) |
| 9.63 | −0.016 (±0.040) |
| 11.3 | −0.025 (±0.050) |

*B. Titration with Ferrocyanide.*—Many metals form slightly soluble ferrocyanides. As we have seen, the potential of the ferri-ferrocyanide electrode depends upon the ratio [Feic] : [Feoc]. Now if we titrate a metal solution with ferrocyanide solution, containing a little ferricyanide,[75] the Feoc is removed until all of the metal is precipitated and the potential of the electrode is strongly positive. At the equivalence-point the ferrocyanide concentration increases rapidly, and a sharp fall in potential occurs.

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[73] E. Müller, Z. anorg. Chem., **135**, 265 (1924).

[74] J. B. Conant, J. Biol, Chem., **57**, 401 (1923).

[75] Galetti, Bull. soc. chim., [2], 83 (1864); Z. analyt. Chem., **4**, 213 (1865).

Unfortunately, the method is limited in application because some metals give precipitates of inconstant composition.

The potassium ferrocyanide is readily purified by recrystallization from water and drying over calcium chloride in a desiccator. At constant weight the composition of the salt is $K_4Fe(CN)_6 \cdot 3H_2O$. A $\frac{1}{40}$ molar solution in water containing 1 per cent potassium ferricyanide is a suitable reagent. Kolthoff's experience shows that the solution is stable for a long time when protected from direct sunlight by being placed in a dark brown glass bottle.

*Titration of Zinc*:

$$3Zn^{++} + 2Feoc^{\equiv} + 2K^{+} \rightleftarrows K_2Zn_3(Feoc)_2.$$

The ordinary titration method of Galetti (*loc. cit.*), improved by de Koninck and Prost,[76] which involves the use of a uranyl salt as external indicator (spot plate), is inaccurate in dilute solution. Therefore Knauth [77] showed that the titration might be made by the potentiometric method. This was confirmed quite independently by F. R. von Bischowsky.[78] G. Hedrich [79] made a special study of this titration, and concluded that the method gave highly accurate results. This was not confirmed by Kolthoff,[80] who found that the potential break occurred before the equivalence-point was reached.

Fr. Müller [81] repeated a part of the work of Hedrich and found a deviation of + 0.2 per cent to − 0.3 per cent from the theoretical at room temperature and at 75°. As the zinc titration is of great practical importance, I. M. Kolthoff and E. J. A. H. Verzijl [82] made a special study of the absolute accuracy of the method, and confirmed Kolthoff's former results. The titration may be made at room temperature or at 65°. In the latter case the titration can be finished in a shorter time than at room temperature, although in all cases the potential very slowly reaches a constant value near the equivalence-point. With an excess of ferrocyanide the potential reaches constancy much more rapidly, and hence in some cases it might be advantageous to add an excess of ferrocyanide and titrate back with zinc solution.

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[76] de Koninck and Prost, Z. angew. Chem., **9**, 460, 564 (1896).

[77] Knauth, Dissertation, Dresden (1915).

[78] F. R. von Bischowsky, J. Ind. Eng. Chem., **9**, 668 (1917).

[79] G. Hedrich, Studien zur elektrometrischen Titrationen von Zink, u. s. w., Dissertation, Dresden (1919).

[80] I. M. Kolthoff, Rec. trav. chim., **41**, 425 (1923).

[81] Fr. Müller, Z. anorg. Chem., **128**, 126 (1923).

[82] I. M. Kolthoff and E. J. A. H. Verzijl, Rec. trav. chim., **43**, 380 (1924).

The direct titration of zinc with ferrocyanide requires at least half an hour even at 65°. E. Müller and K. Gäbler [83] recommend that the titration be carried to an inflection-potential of + 0.30 volt. Since the reaction is slow near the equivalence-point the danger of over-titrating is very great; another disadvantage is that the inflection-potential is very dependent upon the composition of the solution. Acids decrease the break at the end-point.

With regard to the accuracy of the titration, Kolthoff and Verzijl (*loc. cit.*) found the following values in the titration of 100 cc. of 0.1 N zinc sulphate:

ACCURACY OF THE ZINC TITRATION

| Temperature During Titration | Electrolyte Added | Error in Per Cent of Cubic Centimeters of Required Reagent |
|---|---|---|
| 15° | (neutral) | −1.04 |
| 65° | .............................. | −0.9 |
| 15° | 0.12 N sulphuric acid | −0.77 |
| 65° | 0.12 N sulphuric acid<br>+3 g. potas. sulphate | −0.4 |
| 65° | 5 g. potas. sulphate | −0.45 |
| 15° | 10 g. ammonium chloride | −2.25 |
| 65° | 10 g. ammonium chloride | −0.8 |
| 15° | 20 g. ammonium sulphate | −0.05 |
| 65° | 20 g. ammonium sulphate | −1.15 |

It may be concluded from these results that the error is about

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[83] E. Müller and K. Gäbler, Z. analyt. Chem., **62**, 29 (1923).

−1 per cent in neutral solution at room temperature, or at 65°. Addition of potassium sulphate improves the result; theoretical results are obtained when a large amount of ammonium sulphate is added and the titration is at room temperature. The long time required is a disadvantage in this case. At 65° the ammonium sulphate causes an error of − 1.1 per cent.

In agreement with Hedrich (*loc. cit.*), Kolthoff and Verzijl (*loc. cit.*) found the influence of ammonium chloride to be very peculiar. At room temperature it causes an error of − 2.2 per cent; at higher temperature it has no influence. They also found that a large amount of calcium chloride causes an error of − 2.5 per cent, and magnesium sulphate one of − 1.5 per cent. Small quantities of these salts have no influence. Large amounts of aluminum salts make the electrode insensitive. Manganese has a disturbing action because it forms a slightly soluble double salt with ferrocyanide. It must therefore be removed from solution, preferably by precipitation as manganese dioxide by persulphate in slightly acid solution. Iron salts interfere. Ferric iron may be rendered harmless by the addition of an excess of ammonium fluoride to the slightly acid solution. *In this way zinc may be titrated in the presence of iron* (Kolthoff and Verzijl). Ferrous iron must be oxidized before titration. Copper and cadmium salts must be separated from the zinc prior to the titration.

W. D. Treadwell and D. Chervet [84] stated that the composition of a metal ferrocyanide depends upon the alkali metal of the ferrocyanide. They found, for example, that in titrating zinc with potassium ferrocyanide the precipitate had the composition, $K_2Zn_3(Feoc)_2$, while the sodium ferrocyanide $Zn_2Feoc$ was formed. In the presence of caesium or rubidium $ZnX_2(Feoc)_2$ is formed (X = Cs or Rb), and the break in potential is much greater than in the absence of these salts.

Kolthoff and Verzijl [85] obtained a peculiar titration curve when caesium was present. They explain the peculiarities of the curve as being due to the formation of a slightly soluble zinc-caesium ferricyanide of the composition $2\ Zn_3(Feic)_2Cs_3Feic$. In direct contradiction to Treadwell and Chervet, they did not note any influence of rubidium chloride on the titration curve of zinc. In agreement with Treadwell and Chervet, they found that sodium ferrocyanide formed $Zn_2Feoc$, which, however, is transformed into $Na_2Zn_3(Feoc)_2$ by an excess of this reagent. A similar result was obtained with hydroferrocyanic acid instead of the sodium salt, whereas Treadwell and Chervet state that pure zinc ferrocyanide is formed in this case. Kolthoff and Verzijl found two jumps in the potential curve when magnesium ferrocyanide was the reagent in acid solution: the first corresponding to the formation of $Zn_2Feoc$, and the second to $MgZn_3(Feoc)_2$. Calcium ferrocyanide gave similar results in neutral solution, whereas barium ferrocyanide formed the pure salt, $Zn_2Feoc$.

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[84] W. D. Treadwell and D. Chervet, Helv. Chim. Acta, **5**, 633 (1922); **6**, 550,559 (1923).

[85] Kolthoff and Verzijl, Rec. trav. chim., **43**, 388, 393 (1924); *cf.* also Fr. Müller, Z. anorg. Chem., **128**, 125 (1923).

F. Fenwick [86] has applied the bimetallic system in the titration of zinc with potassium ferrocyanide. The original potential difference is high on account of the irreversible nature of the potential of zinc on platinum. " The end-point is marked by a fall in potential during the addition of a rather larger volume of the titrating solution than is the case in determinations employing a stronger reducing (or oxidizing) agent." The point of maximum rate of change in potential is easy to detect. Miss Fenwick does not state the absolute accuracy of the method.

*Determination of Cadmium.*—In the titration of a cadmium salt with potassium ferrocyanide, the break in potential does not occur exactly at the point corresponding to the formation of $K_2CdFeoc$ (Hedrich, *loc. cit.*). The deviation becomes smaller as the solution becomes more dilute. In 0.001 N solution, pure $K_2CdFeoc$ is precipitated. According to Treadwell and Chervet (*loc. cit.*) the addition of a caesium or rubidium salt improves the result; this statement was not confirmed by Fr. Müller (*loc. cit.*). In agreement with Müller, Kolthoff and Verzijl stated that the titration of cadmium with ferrocyanide did not yield exact results. When sodium ferrocyanide is used instead of the potassium salt, pure cadmium ferrocyanide is precipitated (Treadwell and Chervet). According to Fr. Müller, accurate results are obtained.

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[86] F. Fenwick, Dissertation, Ann Arbor, Mich. (1923), p. 80.

*Zinc and Cadmium in the Same Solution.*—According to Hedrich (*loc. cit.*) there are two jumps in potential, one corresponding to the complete precipitation of zinc as $K_2Zn_3(Feoc)_2$, and the second to $K_2CdFeoc$. Kolthoff (unpublished data) did not succeed in obtaining good results. Fr. Müller used sodium ferrocyanide, but failed to improve the method in this way.

*Determination of Lead*:

$$2Pb^{++} + Feoc^{\equiv} \rightleftarrows Pb_2Feoc.$$

According to E. Müller and K. Gäbler [87] the direct titration of lead with ferrocyanide gives good results when the lead concentration is larger than 0.01 molar. In dilute solution too little reagent is required to reach the inflection-point. Kolthoff was able to confirm these results. When the titration is performed at 75° the potentials soon become constant. Inflection-potential, + 0.18 volt (against N.C.E.). In the presence of large amounts of acetate the determination is no longer practicable, because of the formation of complex lead acetate. F. Fenwick (*loc. cit.*) has applied the bimetallic system, and recommends the titration of a cold solution.

*Separate Precipitation of Zinc and Lead.*—In the titration of a mixture of zinc and lead salt with potassium ferrocyanide, the first potential break occurs after precipitation of the zinc, and the second after the lead ferrocyanide is formed quantitatively. The titration is not practicable, however. Therefore Müller and Gäbler recommend the titration for the sum of the metals at 75° (inflection-potential, + 0.19 volt). Another titration is made in which the zinc alone is precipitated, after previous removal of lead by a slight excess of sulphuric acid; inflection-potential, + 0.50, if titration is at 75°.

*Determination of Sulphate.*—E. Müller and R. Wertheim [88] add an excess of lead nitrate to the sulphate solution; a third of the volume of the solution must be alcohol. The precipitate is filtered, washed with 30 per cent alcohol, and the excess of lead in the filtrate is determined with potassium ferrocyanide. The method is not convenient for practical use.

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[87] E. Müller and K. Gäbler, Z. analyt. Chem., **62**, 29 (1923).

[88] E. Müller and R. Wertheim., Z. anorg. Chem., **133**, 411 (1924).

In another paper Müller and Wertheim [89] have described the application of the method to the determination of barium. The results are not very accurate.

Kolthoff (unpublished investigation) has applied the lead ferrocyanide-ferricyanide electrode for the direct titration of sulphate (*cf.* Part I, p. 126). He adds to the sulphate solution a little solid lead ferrocyanide and about 50 mg. ferricyanide, and an equal volume of alcohol. The titration is carried out with lead nitrate. A break in potential occurs exactly at the point where lead sulphate is quantitatively formed. In the absence of alcohol the potential is very unsteady. The titration has not yet been studied with various salts present.

The ferrocyanide titration is not suitable for the determination of silver or copper; [90] nor of cobalt (F. Fenwick, *loc. cit.*).

**7. Reduction with Ferrous Sulphate.**—*Determination of Chromium and Vanadium.*—The theoretical aspects of the bichromate-ferrous iron titration have been thoroughly discussed in § 2 of this chapter (p. 248). A number of practical applications, which rest chiefly on the work of G. L. Kelley and his collaborators, will now be described.

Kelley, Adams, and Wiley [91] have described a simple form of apparatus, which is essentially a simple potentiometer with a lamp and scale galvanometer (*cf.* Figs. 19 and 22). Because of certain irreversible phenomena (*cf.* § 2, especially the work of Forbes and Bartlett) the end-point may be taken as a sudden large galvanometer deflection which throws the beam of light permanently beyond the ground-glass scale. This procedure has met with much favor for rapid industrial determinations.

In most practical instances, vanadium and chromium may be found together in the solution of various steels, ferro-alloys, etc.

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[89] E. Müller and R. Wertheim, Z. anorg. Chem., **135**, 269 (1924).

[90] *Cf.* Müller, Die Elektrometrische Massanalyse, 2d Ed., p. 123.

[91] G. L. Kelley, J. R. Adams, J. A. Wiley, J. Ind. Eng. Chem., **9**, 780 (1917).

*Vanadate.*—If the solution contains vanadium alone, the reaction with ferrous iron is:

$$VO_4^{\equiv} + 6H^+ + Fe^{++} \rightleftarrows VO^{++} + Fe^{+++} + 3H_2O.$$

Partial reactions:

$$VO_4^{\equiv} + 6H^+ + \ominus \rightleftarrows VO^{++} + 3H_2O; \quad \varepsilon_0 = +0.916$$

$$Fe^{++} \rightleftarrows Fe^{+++} + \ominus; \quad \varepsilon_0 = +0.466.$$

The potentiometric vanadate reduction has been studied by Kelley and his collaborators (*vide infra*), by Willard and Fenwick [92] and by Kolthoff and Tomicek.[93] We may conclude from these investigations that the titration gives very exact results.

*Determination of Chromium.*—If chromium alone is present, its oxidation is effected by means of ammonium persulphate and silver nitrate in the sulphuric acid solution of the alloy. The excess of persulphate is destroyed by boiling. Any permanganic acid that is formed is also destroyed by boiling after the addition of hydrochloric acid. The chromium is then determined by titration with ferrous sulphate, which has been standardized against bichromate solution of known normality.

*Determination of Vanadium.*—If vanadium alone is present, its oxidation may be effected in acid solution by slight excess of permanganate or persulphate. The excess of either oxidant is destroyed by heating. The titration with ferrous sulphate is then made.

*Chromium and Vanadium.*—When both elements are present, the selective oxidation of either is a matter of considerable difficulty because both have about the same normal potential. The sum of the two elements is determined by titration with ferrous sulphate after both have been oxidized with persulphate or permanganate.

Kelley *et al.*[94] then determine vanadium by reduction with standard ferrous sulphate, after previous oxidation of the vanadium with nitric acid. The original volume of the solution is 100–125 cc.; 40 cc. of conc. nitric acid are added, and the solution is boiled for one hour at such a rate that the volume of the solution does not fall below 100 cc. Under these conditions a constant portion, namely 99.5 per cent, of the vanadium is oxidized to vanadic acid. The chromium is unaffected. Hence the volume of ferrous sulphate used is multiplied by $\frac{1000}{995}$.

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[92] H. H. Willard, and F. Fenwick, J. Am. Chem. Soc., **45**, 84 (1923).

[93] I. M. Kolthoff and O. Tomicek, Rec. trav. chim., **43**, 447 (1924).

[94] G. L. Kelley and J. B. Conant, J. Am. Chem. Soc., **38**, 341 (1916); J. Ind. Eng. Chem., **9**, 780 (1917); G. L. Kelley, J. A. Wiley, R. T. Bohn, and W. C. Wright, J. Ind. Eng. Chem., **13**, 939 (1921).

Kelley and his co-workers have studied the application of these methods to the examination of special steels (*loc. cit.*), ferrochromium,[95] and ferrovanadium.[96]

## Procedures

*A. Chromium in Steel* (*Vanadium Absent*).[97]—From 0.5 to 2.0 g. of steel, depending on the amount of chromium present, is dissolved in 60–100 cc. of sulphuric acid (sp. gr. 1.20). The solution is evaporated until salts begin to separate, in order to decompose carbides. After dilution to about 50 cc. the hot solution is treated with 2–3 cc. of nitric acid.[98] The solution is diluted to 250–300 cc. and kept at boiling temperature. Ten cubic centimeters of 0.015 N silver nitrate and a solution of 5.0 g. of ammonium persulphate are added. The solution is boiled vigorously for ten minutes, after which 5 cc. of (1 : 3) hydrochloric acid are added and boiling is continued for five minutes longer. After cooling and addition of a little sulphuric acid, the solution is titrated with standard ferrous sulphate.

*B. Chromium in Chrome-vanadium Steel.*—The procedure given above oxidizes both chromium and vanadium (Section *A*). The number of cubic centimeters of ferrous sulphate found in the titration represents chromium and vanadium. Hence the amount of ferrous sulphate equivalent to the vanadium alone must be determined (as described in the following section, *C*) and deducted from the total. The per cent of chromium may then be calculated.

*C. Vanadium in Chrome-vanadium Steel.*[99]—"When the amount of vanadium is less than 0.5 per cent, dissolve a 2.0-g. sample in 100 cc. of sulphuric acid (sp. gr. 1.20). With higher percentages of vanadium use a 1.0-g. sample and dissolve in 80 cc. of sulphuric acid of sp. gr. 1.20. When solution is complete add nitric acid, drop by drop, to the amount of 2 cc.

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[95] G. L. Kelley and J. A. Wiley, J. Ind. Eng. Chem., **13**, 1053 (1921).

[96] G. L. Kelley, J. A. Wiley, R. T. Bohn, and W. C. Wright, J. Ind. Eng. Chem., **13**, 939 (1921).

[97] Kelley and Conant, J. Ind. Eng. Chem., **8**, 722 (1916).

[98] If visible particles of carbide remain, treatment with aqua regia, followed by complete expulsion of hydrochloric acid, is usually successful in effecting solution.

[99] Kelley, Wiley, Bohn, and Wright, J. Ind. Eng. Chem., **11**, 633 (1919).

Boil until oxides of nitrogen are removed and until the tungstic acid is yellow if there is any present. Dilute the solution with hot water to a volume of 100 to 125 cc. and add 40 cc. of conc. nitric acid. Boil the solution during one hour or more at such a rate that the volume does not fall below 100 cc. Cool, dilute to 300 cc., and titrate at 20° C. or lower with ferrous sulphate and dichromate solution. For this purpose a solution of dichromate may be prepared by dissolving 0.9609 g. of potassium dichromate in a liter of water. . . . One cubic centimeter of this dichromate solution is equivalent to 0.1 per cent of vanadium in a 1.0 g. sample.

"The titration of the nitric acid solution of the oxidized vanadium corresponds to 99 per cent of the vanadium present. Accordingly this may be calculated by dividing by 0.99, or approximated by adding 1 per cent of the amount found in the titration." [100]

*D. Chromium in Ferrochromium.*[101]—"Use a nickel crucible of about 60-cc. capacity, preferably free from manganese. Fuse 20 g. of sodium carbonate in the crucible, and during cooling rotate it in such a manner as to produce a lining on the crucible. When cool, place 16 g. of sodium peroxide in the crucible. Make a hole in the center of this and place in it 1.0 g. of ferrochromium, ground to pass a 100-mesh sieve. Mix the ferro-alloy with the peroxide by stirring with a stiff platinum wire, taking care that the alloy does not sink to the bottom. Fuse over a blast lamp until fusion is complete, and apply heat enough to maintain the melt in a state of quiet fusion for three minutes, rotating gently meanwhile. Avoid fusing the lining as this is detrimental to the crucible. During cooling, cause the molten mass to flow in thin layers on the surface of the crucible. When cold, wipe the outside of the crucible clean, and place it in 300 cc. of water in a 600-cc. beaker. Warm to complete the solution of the mass, and remove the crucible after rinsing. Boil the solution at least thirty minutes. Cool to room temperature, and add gradually 80 cc. of sulphuric acid (sp. gr. 1.58). Boil five minutes, cool, filter through asbestos, and make the volume up to exactly one liter. Analyze the solution as soon as it is prepared. Remove a 100-cc. portion, add 25 cc. of sulphuric acid, and titrate electrometrically with ferrous ammonium sulphate and potassium dichromate."

If the dichromate solution contains 5.6586 g. of dichromate per liter, each cubic centimeter will represent 2.00 per cent chromium on a 0.10-g. sample. Convert the cubic centimeters of ferrous sulphate into their equivalent in terms of dichromate.

"Vanadium is rarely present in ferrochromium in quantities warranting its determination. When it is desirable to determine it, this may be done, after reduction of the chromate and vanadate with ferrous sulphate, by oxidizing the vanadium alone by means of nitric acid. It is then titrated electrometrically with ferrous sulphate."

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[100] In a subsequent paper these investigators found that 99.5 per cent of the vanadium was oxidized by the nitric acid, J. Ind. Eng. Chem., **13**, 939 (1921).

[101] Kelley and Wiley, J. Ind. Eng. Chem., **13**, 1053 (1921).

*E. Vanadium and Chromium in Ferrovanadium.*[102]—"Dissolve 3.0 g. of ferrovanadium in 75 cc. of nitric acid (sp. gr. 1.13). When solution is nearly complete, add 10 cc. of hydrochloric acid (sp. gr. 1.20). When the amount of silicon is large, it may be convenient to add a few drops of hydrofluoric acid to bring about solution. Next add 50 cc. of sulphuric acid (sp. gr. 1.58) and evaporate until fumes appear, to remove nitric and hydrochloric acids, and to complete the decomposition of vanadium carbides. . . . The solution is then cooled and made up to 1000 cc. one-hundred-cubic centimeter portions of this solution, corresponding to 0.3 g., are convenient quantities for subsequent work."

*Determination of Vanadium and Chromium.*—After oxidation with ammonium persulphate, the quantity of standard ferrous sulphate which is necessary to reduce both chromate and vanadate is found. The procedure is exactly as described in Section *A* above.

*Vanadium.*—A separate 100-cc. portion of the solution is used for the determination of vanadium. Selective oxidation of the vanadium with nitric acid, followed by potentiometric titration of the vanadic acid with ferrous sulphate, is carried out exactly as described in Section *C*. The volume of ferrous sulphate is multiplied by $\frac{1000}{995}$ to allow for the incomplete oxidation of the vanadium by the nitric acid. The corrected volume is deducted from the volume for both chromium and vanadium, in order that the per cent of chromium may be calculated.

According to Willard and Fenwick,[103] the selective reduction of chromic acid in the presence of vanadic acid is accomplished by sodium perborate (or by very pure hydrogen peroxide) in a solution whose acidity is controlled by the presence of large amounts of acetic acid and sodium acetate. They studied the application of this method to the potentiometric determination of vanadium and chromium in special steels and ferro-alloys, with excellent results. The polarized bimetallic system was used.

Furman [104] has studied the method of Willard and Fenwick for the selective reduction of chromium and found it to be highly satisfactory. In this study diphenylamine was used as indicator instead of the potentiometric method.

### PROCEDURES

*Vanadium in Chromium-vanadium Steel.*—"A sample requiring about 10 cc. of 0.02 N ferrous sulphate is convenient. Place it in a 600-cc. beaker, add 20 to 30 cc. of water and run in a measured volume of conc. sulphuric acid from a burette. Each gram of steel requires 1 cc. of the acid to form ferrous sulphate and a 4-cc. excess is sufficient to effect a rapid solution. Heat gently until the sample is dissolved and salts begin to separate. Dilute with 20 cc. of hot water and heat until dissolved. Add 4 or 5 cc. of conc. nitric acid cautiously and boil. Complete the oxidation of iron and vanadium with a slight excess of potassium permanganate. Add sufficient sodium acetate (a moderate excess does no harm), to combine with the acid used in excess of that required for solution (1 cc. of conc. sulphuric acid, = 4.8 g. of sodium acetate trihydrate), and 40 to 50 cc. of glacial acetic acid. Add about 0.5 g. of sodium perborate, previously neutralized (with acetic acid); dilute, if necessary, to 200 cc. and boil for twenty minutes. Cool to room temperature, add 25 to 30 cc. of conc. hydrochloric acid and titrate with 0.02 N ferrous sulphate solution standardized against permanganate."

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[102] Kelley, Wiley, Bohn, and Wright, J. Ind. Eng. Chem., **13**, 939 (1921).

[103] H. H. Willard and F. Fenwick, J. Am. Chem. Soc., **45**, 84 (1923).

[104] N. H. Furman, Ind. Eng. Chem., **17**, 315 (1925).

*Vanadium in Chromium-vanadium-tungsten Steel.*—"Treat the samples with 40 cc. of hydrochloric acid, 3 parts conc. acid to 1 of water, and heat until action ceases. Add 8 to 10 cc. of conc. nitric acid, dropwise, until the first violent action has ceased. Boil and evaporate to about 20 cc. Dilute with hot water and heat to insure complete solution of soluble salts. Filter and wash with hot 2 per cent hydrochloric acid. Oxidize the filtrate with permanganate solution and add sufficient sodium acetate to combine with the free acid. This may be estimated accurately enough by putting the weight of the hydrochloric acid as equal to 20 per cent of the volume after concentrating the solution to about 20 cc. and adding 5 or 6 g. more as a safeguard; 1 g. hydrochloric acid = 3.73 g. sodium acetate trihydrate. From here the determination is carried on as outlined above.

"To determine the vanadium occluded by the tungstic acid, dissolve the latter in sodium carbonate. Add a few tenths of a gram of perborate and boil vigorously for ten minutes. Acidify with 3 to 5 cc. of phosphoric acid, add 25 to 40 cc. of sulphuric acid (1 part of acid to 3 of water) and titrate with ferrous sulphate electrometrically to the permanent drop in potential."

*Vanadium in Molybdenum-chromium-vanadium Steel.*—Proceed exactly as described under Chromium-vanadium Steel.

Willard and Fenwick (*loc. cit.*) have found that the vanadium which is present in a phospho-molybdate precipitate may be determined exactly as described above under the determination of vanadium occluded by tungstic oxide.

Kolthoff and Tomicek [105] determine the previously oxidzed chromium and vanadium together by reduction with ferrous sulphate solution. The customary oxidation-potential system is used. They found that the slight excess of ferrous iron could then be titrated with permanganate, giving one potential break. A second jump occurs at the completion of the oxidation of the vanadyl salts. The titration is made at 70°; chromic salts are not oxidized. Kolthoff and Tomicek studied the accuracy of the vanadium reduction in the presence of large quantities of iron. They found that with 1V : 1000 ferric iron the results were satisfactory, although the E.M.F. readings near the equivalence-point were sometimes irregular.

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[105] I. M. Kolthoff and O. Tomicek, Rec. trav. chim., **43**, 447 (1924).

### Procedure for Steels

A sample of suitable weight, according to the content of chromium and vanadium, is decomposed by repeated treatments with nitric acid. The nitric acid and nitrates are decomposed by strong heating with excess of sulphuric acid. After dilution and filtration the residue is subjected to acid treatment, or alkali fusion, if necessary. Any nitrates or chlorides introduced in the treatment are expelled with excess of sulphuric acid. The solution is now diluted to the mark in a suitable volumetric flask. One aliquot portion is used for the vanadium determination, and a second portion for the combined chromium and vanadium determination.

(1) *Vanadium.*—A portion of the solution will ordinarily give a potential of less than 0.5 volt (cell composed of platinum electrode—normal calomel electrode). If this is not the case, add ferrous sulphate in slight excess. Add enough sulphuric acid to make the solution 1 N in acid. Dilute to 150 to 200 cc. Titrate with 0.05 N permanganate (or with 0.02 N if the vanadium content is extremely small) at 18° until the oxidation of ferrous iron is complete, then at 75°–80° until the vanadium is completely oxidized, as indicated by a second inflection.

(2) *Chromium and Vanadium.*—A second aliquot portion of the steel solution, which need be only moderately acid, is treated with 1 to 5 g. of potassium persulphate, diluted to 150 cc. in an Erlenmeyer flask and heated to boiling. Cool after boiling for fifteen minutes. Remove any precipitated peroxide of manganese by filtration, and dilute the clear solution as above described (1). If the solution is colored by permanganic acid titrate carefully to the first inflection. Titrate with 0.05 or 0.02 N

ferrous sulphate solution until the chromic and vanadic acids have been reduced. The end of the reduction is indicated by a sharp inflection.

*Use of the Bichromate-Ferrous Sulphate Reaction in the Determination of Tellurium.*—W. T. Schrenk and B. L. Browning [106] oxidize tellurous acid to telluric with a measured excess of potassium bichromate. After standing 45–60 minutes, the amount of oxidizing agent required is found by potentiometric determination of the excess of bichromate with standardized ferrous sulphate solution. Accurate results were obtained for 0.2–0.4 g. of $TeO_2$, when as much as 0.278 g. $SeO_2$ or 0.03 g. Cu was present.

**8. Reduction with Iodide.**—The reader is referred to preceding paragraphs in this chapter for the reactions between iodide and permanganate, dichromate,[107] bromate, or iodate.

For the determination of *Iodate*, W. S. Hendrixson [108] recommends the addition of an excess of known iodide solution in dilute sulphuric acid, and the titration of the excess with permanganate solution.

E. Müller and D. Junck [109] made a study of the theoretical aspects of the titration curve of iodate with iodide. In sulphuric acid medium, only one jump in potential occurs, at the end of the reduction of all iodate:

$$IO_3^- + 5I^- + 6H^+ \rightleftarrows 3I_2 + 3H_2O.$$

Inflection-potential, 0.652 (or 0.580?) volt (against N.C.E.).

In the presence of hydrochloric acid other reactions occur. The first break in potential is obtained after the completion of the reaction:

$$IO_3^- + 2I^- + 6H^+ + 3Cl^- \rightleftarrows 3ICl + 3H_2O,$$

and a second after:

$$3ICl + 3I^- \rightleftarrows 3I_2 + 3Cl^-.$$

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[106] W. T. Schrenk and W. L. Browning, J. Am. Chem. Soc., **48**, 139 (1926).

[107] *Cf.* esp. W. S. Hendrixson, J. Am. Chem. Soc., **43**, 14 (1921).

[108] W. S. Hendrixson, J. Am. Chem. Soc., **43**, 858 (1921).

[109] E. Müller and D. Junck, Z. Elektrochem., **31**, 200 (1925).

In the presence of a large excess of hydrochloric acid, still different results are obtained. Probably both ICl and $ICl_3$ are both formed:

$$2IO_3^- + I^- + 12H^+ + 9Cl^- \rightleftarrows 3ICl_3 + 6H_2O,$$

$$3ICl_3 + 9I^- \rightleftarrows 6I_2 + 9Cl^-.$$

Because of the escape of chlorine, both breaks occur too soon. This determination of iodate in hydrochloric acid solution is of no analytical significance.

*Periodic Acid.*—In the presence of a large excess of iodide the following action takes place:

$$IO_4^- + 2I^- + 2H^+ \rightleftarrows 2IO_3^- + I_2 + H_2O.$$

The iodate is not reduced further in bicarbonate solution. According to Müller and Junck (*loc. cit.*), the reduction is so slow that the reaction can not be made a basis for potentiometric titration. The present authors suggest the use of an excess of iodide and back titration with silver nitrate or a mercuric salt.

*Hypochlorite.*—W. D. Treadwell[110] makes the Pontius method the basis of the potentiometric determination of hypochlorite:

$$3OCl^- + I^- \rightleftarrows IO_3^- + 3Cl^-.$$

The titration gives practicable results in bicarbonate solution, or in the presence of boric acid.

According to Treadwell the method is of distinct advantage in titrating very dilute solutions. Kolthoff[111] was able to confirm Treadwell's findings. Initially the potential soon becomes constant; near the equivalence-point, however, one has to wait about ten minutes for it to reach constancy. The break in potential is distinct, but not nearly as pronounced as in the titration of hypochlorite with arsenic trioxide. (*Cf.* § 9.) Chlorite reacts very slowly with iodide in bicarbonate solution.

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[110] W. D. Treadwell, Helv. Chim., Acta, **4**, 396 (1921).

[111] I. M. Kolthoff, Rec. trav. chim., **41**, 740 (1922).

**9. Reduction with Arsenic Trioxide.**—Arsenic trioxide may be readily purified by sublimation or reprecipitation from its alkaline solution upon adding acid, followed by recrystallization. Its solution may be kept for a long time when it is neutral or slightly acid. An alkaline solution is slowly oxidized by air, thus decreasing its strength.

*Hypochlorite.*—According to W. D. Treadwell [112] the method of Penot (1851) may be applied as a potentiometric titration. A good end-point is obtained when the titration is carried out in bicarbonate medium. No inflection is observed in strongly alkaline medium. Good results are obtained when the amount of bicarbonate present suffices to neutralize the strong alkali to carbonate. I. M. Kolthoff (*loc. cit.*), using the usual system, confirmed Treadwell's results. He found that chlorite did not react with arsenious oxide under the conditions mentioned. No sharp end-point was obtained in weakly acid solution.

A. Schleicher and L. Toussaint [113] used the compensation apparatus of A. Fischer [114] and titrated to an inflection-potential of 0.60 volt (against N.C.E.). A platinum electrode in dilute peroxide, or $\frac{M}{5}$ dichromate, may also be used as a compensation electrode.

According to Kolthoff (*loc. cit.*) the sum of the chlorite and hypochlorite is determined by iodometric titration in acid solution. When the hypochlorite content is known, that of chlorite may be calculated.

The application of the bimetallic system to the titration of hypochlorite also gives good results, according to F. Fenwick.[115]

*Bromate.*—On page 256 the authors discussed the titration of arsenic with bromate, according to Zintl and Wattenberg.[116] F. Fenwick (*loc. cit.*) has applied the bimetallic system. "Bromate is rapidly reduced by arsenite in hydrochloric acid solution.

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[12] W. D. Treadwell, Helv. Chim. Acta, **4**, 396 (1921).

[113] A. Schleicher and L. Toussaint, Z. analyt. Chem., **65**, 399, 406 (1925).

[114] A. Fischer, Elektroanalytische Schnellmethode, Stuttgart (1908), p. 100.

[115] F. Fenwick, Dissertation, Ann Arbor, Mich. (1923), p. 83.

[116] Zintl and Wattenberg, Ber., **56**, 472 (1923).

The end-point is marked by the usual rise in voltage followed by a fall in the presence of an excess of titrating agent. The end-point increases in speed and sharpness with the concentration of hydrochloric acid, but is readily obtainable in a concentration as low as 5 per cent. If the concentration of hydrochloric acid does not rise over 8 per cent a selective titration of bromate may be made in the presence of any quantity of chlorate."

*Hypobromite.*—According to H. H. Willard and F. Fenwick [117] the titration of hypobromite solution with arsenite gives an excellent end-point with both mono- and bi-metallic electrode systems. When polarized electrodes are used the potential difference increases slowly as the end-point is approached; the inversion is sharp and the subsequent fall can not be mistaken. These investigators obtained good results even in strongly alkaline solution.

*Determination of Iodide.*—Willard and Fenwick applied the method to this determination. They state that: When hypobromite is added to a neutral or alkaline solution of an iodide no change occurs at first, but after considerable hypobromite has been added the yellow color of the solution fades. A direct titration of iodide with hypobromite was not found to be possible because of the slowness of the reaction. They therefore add an excess of hypobromite to the alkaline iodide solution, dilute to 100 cc. and titrate the excess with arsenite after the solution has stood five minutes.

$$I^- + 3OBr^- \rightleftarrows IO_3^- + 3Br^-.$$

The hypobromite has no oxidizing action on bromide or chloride. The solution is made by pouring 40 to 50 g. of bromine slowly into a solution of 30 g. of potassium hydroxide in 250 cc. of water kept near 0° C., and diluting finally to 5 liters. The solution is standardized against arsenite.

The potentiometric titration of iodine with arsenious oxide has been described by C. S. Robinson and O. B. Winter.[118]

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[117] H. H. Willard, and F. Fenwick, J. Am. Chem. Soc., **45**, 631 (1923).

[118] C. S. Robinson and O. B. Winter, J. Ind. Eng. Chem., **12**, 775 (1918).

**10. Use of Mercurous Nitrate for the Determination of Manganese.**—For the determination of manganese in steel, G. L. Kelley *et al.*[119] perform the oxidation with sodium bismuthate, thus forming permanganic acid. The latter is titrated with mercurous nitrate, a reagent which has the advantage of reducing permanganate quantitatively and rapidly at ordinary temperatures without reducing chromates or vanadates which are also formed by the bismuthate oxidation. The reduction may be represented by the equation:

$$4\mathrm{Mn^{VII}} + 14\mathrm{Hg^{I}} \rightleftarrows 3\mathrm{Mn^{IV}} + \mathrm{Mn^{II}} + 14\mathrm{Hg^{II}},$$

or

$$4\mathrm{MnO_4}^- + 7\mathrm{Hg_2}^{++} + 20\mathrm{H}^+ \rightleftarrows$$
$$3\mathrm{MnO_2} + \mathrm{Mn}^{++} + 14\mathrm{Hg}^{++} + 10\mathrm{H_2O}.$$

This is the sum of the two simpler reactions:

$$2\mathrm{Mn^{VII}} + 6\mathrm{Hg^{I}} \rightleftarrows 2\mathrm{Mn^{IV}} + 6\mathrm{Hg^{II}},$$

and

$$2\mathrm{Mn^{VII}} + 8\mathrm{Hg^{I}} \rightleftarrows \mathrm{Mn^{IV}} + \mathrm{Mn^{II}} + 8\mathrm{Hg^{II}},$$

either of which might have been expected to occur more readily than the complicated reaction above. (*Cf.* original paper for a detailed discussion of this interesting reaction.)

When the solution contains chromates and vanadates, the titration is best carried out in the presence of a moderately high concentration of sulphuric acid. Kelley *et al.* used 50 cc. of acid of sp. gr. 1.58 and 200 cc. of water. With a lower acid concentration, manganese dioxide separates from the solution and erratic results are found in the titration. Nitric acid does not interfere if it be first freed of nitrous acid. This is best accomplished by treating the acid with a small excess of sodium bismuthate and filtering to remove the excess. The temperature of the solution should be close to 20° C. At higher temperatures a larger amount of mercurous nitrate is used, undoubtedly because of partial reoxidation of manganese. At low temperatures this reaction proceeds so slowly that it does not give trouble.

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[119] G. L. Kelley, M. G. Spencer, C. B. Illingworth, and T. Gray, J. Ind. Eng. Chem., **10**, 19 (1918).

The mercurous nitrate solution is prepared by dissolving 10.5 g. of the salt in 150 cc. of water to which 2 cc. of nitric acid have been added. Any undissolved salt is removed by decantation, and the solution is made up to a volume of 1 liter. Its strength is determined potentiometrically with a solution of permanganate which has been standardized against sodium oxalate. The permanganate solution contains 0.5 g. of manganese per liter. The Kelley single-deflection end-point is used in the titrations (*cf.* § 7, p. 273).

### Procedures

*Standardization of Mercurous Nitrate.*—The solution is standardized by using it to reduce portions of potassium permanganate solution; the end-point is determined potentiometrically.

*Potassium Permanganate Solution.*—A solution of 1.5 g. potassium permanganate is allowed to stand several days. It is filtered through asbestos. Its strength is determined with sodium oxalate. The solution is then diluted until it contains 0.0005 g. manganese per cubic centimeter (i.e., 0.1200 g. pure sodium oxalate require 39.33 cc. of the adjusted permangate).

*1. Determination of Manganese after Oxidation with Sodium Bismuthate.*—"The oxidation is carried out exactly as described by Blair.[120] After filtering, a small piece of ice is added, followed by 50 cc. of sulphuric acid (sp. gr. 1.58). The volume should be 250 cc. and the temperature not over 40° C. at the time of titration."

*2. Determination of Manganese after Oxidation with Ammonium Persulphate.*—"Dissolve 0.5 g. steel in 65 cc. sulphuric acid of sp. gr. 1.20." (If manganese is below 0.5 per cent a 1.0-g. sample may be used.) "When solution is complete, oxidize with nitric acid added dropwise. After boiling a minute or two, the solution is diluted with hot water to a volume of 200 cc., heated to boiling, and 10 cc. of silver nitrate solution (2.5 g. in a liter) and 20 cc. of ammonium persulphate solution (100 g. in a liter) added. Boiling is allowed to continue one minute when the solution is allowed to cool slowly, or rapidly with the aid of ice, according to convenience. When the solution is nearly cool enough, a little more sulphuric acid is added and the solution adjusted to about 20°. Titration is then made."

**11. Reduction with Sodium Thiosuplhate.**—Y. Rzymkowski[121] uses thiosulphate as reducing agent in the determination of quinone (and quinhydrone). The reaction may be represented by the equations:

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[120] "The Chemical Analysis of Iron," 7th Ed., p. 122.

[121] Y. Rzymkowski, Z. Elektrochem., **31**, 371 (1925).

$$C_6H_4O_2 + 2H^+ + S_2O_3^= \rightleftarrows C_6H_4O_2H_2S_2O_3, \quad . \quad . \quad . \quad (a)$$

$$C_6H_4O_2 + C_6H_4O_2H_2S_2O_3 \rightleftarrows \underset{\text{hydroquinone}}{C_6H_4O_2H_2} + C_6H_4O_2S_2O_3 \ (b)$$

$$C_6H_4O_2S_2O_3 + 2H^+ + S_2O_3^= \rightleftarrows C_6H_4O_2H_2(S_2O_3)_2.$$

From equation (*a*) we see that the quinone is first reduced to hydroquinone monothiosulphuric acid. The latter reacts with quinone to form hydroquinone and quinone monothiosulphuric acid which reacts with a second thiosulphate ion to form hydroquinone dithiosulphuric acid.

The titration is carried out at 30–40° in a medium which contains acetic acid or a little sulphuric acid. (Rzymkowski does not give details regarding the influence of hydrogen-ion concentration upon the shape of the curve.) The thiosulphate is added very slowly, 1 or 2 drops per second; if it is added too fast, too little reagent is required when the jump in potential is reached. Inflection-potential, 0.00 volt (against N.C.E.). A bimetallic electrode system is advantageous in this instance. An electrode of gold and another of iridium are dipped into the solution to be titrated. The electrodes are connected to a capillary electrometer without using the compensating system (Pinkhof system). The deflection of the electrometer is observed during the titration. It reaches its maximum at the equivalence-point.

It is, of course, better in principle to use the Poggendorff method, either with a calomel reference electrode, or with the simple bimetallic system.

**12. Reduction with Titanous Salts.**—*General Considerations.*—Titanous salts are among the strongest reducing agents used in analytical chemistry. The reduction-potential depends to a large extent upon the hydrogen-ion concentration. For example, B. Diethelm and F. Foerster[122] found a value of + 0.120 volt (against normal hydrogen electrode) for the normal potential when the solution was $\frac{1}{20}$ atomic in titanous ion and 4 N in sulphuric acid; in 0.4 N acid the value was − 0.01

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[122] B. Diethelm and F. Foerster, Z. physik. Chem., **62**, 138 (1908).

volt. The potential is also dependent upon the total quantity of titanium, and decreases with increasing titanium content.

I. M. Kolthoff [123] made measurements with a titanous chloride solution which was 0.036 atomic in titanous, and 0.0435 atomic in titanic ions; hence $\frac{[\mathrm{Ti}^{\mathrm{III}}]}{[\mathrm{Ti}^{\mathrm{IV}}]} = 0.83$. Five cubic centimeters of this solution were added to 100 cc. of the liquid. In the following table we see the influence of hydrochloric acid. The measurements were made against the normal calomel electrode.

| Concentration HCl | $\epsilon_c$ | $\epsilon_c$ Corrected for Chloride Influence |
|---|---|---|
| 0.036 N | −0.342 | −0.342 |
| 0.136 N | −0.318 | −0.313 |
| 0.24 N | −0.290 | −0.278 |
| 0.44 N | −0.260 | −0.238 |

The correction for chloride ion which was applied to yield the figures in the third column was derived from a special series of measurements. Kolthoff also determined the reduction potential at low hydrogen-ion concentration by adding a little soda (down to $p_H = 3$), or a buffer mixture. The results are given in the following table.

| Salt Added | $\epsilon_c$ | $p_H$ | Remarks |
|---|---|---|---|
| Soda | −0.378 | 2 | Clear solution |
| Soda | −0.410 | 2.6 | Clear solution |
| Soda | −0.440 | 3.0 | Clear solution |
| 5 g. potassium biphthalate | −0.428 | 3.1 | Brownish green<br>Gelatinous ppt. |
| 5 g. sodium phosphate (primary) | −0.322 | 4.8 | Light violet ppt. |
| 5 g. sodium oxalate | −0.548 | 4.95 | Liquid yellow-brown |
| 5 g. Rochelle salt | −0.508 | 5 | Liquid light yellow |
| 5 g. sodium acetate | −0.564 | 5.5 | Little steel gray ppt. |
| 5 g. sodium nitrate | −0.526 | 5.9 | Liquid almost colorless |
| 5 g. sodium phosphate (secondary) | −0.320 | 6.8 | Violet precipitate |

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[123] I. M. Kolthoff, Rec. trav. chim., **43**, 768 (1924).

It is rather risky to draw definite conclusions from the results in the table. In the cases where a rather large precipitate was formed (experiments with phthalate and phosphate), the composition of the solution is no longer known. If a solution of $p_H$ greater than 4 remains clear, the greater part of the tri- and quadrivalent titanium must be in the form of complexes. From his results Kolthoff concludes that the oxidation-reduction potential of titanic-titanous solution is given by the equation:

$$E = \varepsilon_0 + 0.059 \log \frac{[Ti^{IV}][H^+]}{[Ti^{III}]} \quad \text{at } 25^\circ \text{ C.}$$

$\varepsilon_0$ is equal to + 0.03 volt referred to the normal hydrogen electrode. The fact that the reducing action of a titanous solution increases considerably with decreasing hydrogen-ion concentration is of importance in analysis. For example, while cupric ions are reduced to cuprous in acid solutions, in the presence of an excess of tartrate ions the reaction appears to go one stage farther, i.e., to metallic copper. Bismuth and lead solutions also give an immediate separation of metal upon the addition of titanous solution if an excess of tartrate is present. Titrations of dyestuffs are generally made in tartrate solutions because the oxidation-reduction potentials of dyestuff systems, as well as that of the titanous solution, depend upon hydrogen-ion concentration.

*Reagents.*—Titanous sulphate and titanous chloride are used as reagents. Titanous sulphate may be prepared by the electrolytic reduction of the titanic salt according to Thornton and Chapman.[124]

Titanous chloride is generally brought on the market as a 20 per cent solution in rather concentrated hydrochloric acid. The chief impurity in almost all of these samples is iron, the content of which may vary from a trace to considerable quantities. According to E. Knecht and E. Hibbert,[125] small quantities of ferrous chloride have no effect upon most determinations. It is desirable to work with iron-free solutions for accurate potentiometric titrations. I. M. Kolthoff and O. Tomicek [126] purified their solutions according to E. Polidori.[127]

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[124] W. M. Thornton, Jr., and J. E. Chapman, J. Am. Chem. Soc., **43,** 91 (1921).

[125] E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis" (1925). Published by Longmans, Green & Co., London.

The commercial solution is cooled in a mixture of ice and salt and saturated with a stream of hydrogen chloride gas. It is then allowed to stand in the freezing mixture until as much of the titanous chloride as possible has separated. The violet crystals of $TiCl_3 \cdot 6H_2O$ are collected as quickly as possible by suction and are washed with ice-cold hydrochloric acid. The crystals oxidize rapidly in air. A 20 per cent solution in 20 per cent hydrochloric acid is prepared. Fifty cubic centimeters of this solution are boiled for one minute with 100 cc. of 25 per cent hydrochloric acid; after cooling, the mixture is made up to 2¼ liters, transferred to a stock bottle, and so preserved that it can not be attacked by air.

It is quite easy to detect the presence of iron qualitatively. A little of the solution is boiled with nitric acid. On cooling, the presence of ferric ion can be detected by the thiocyanate reaction. The purified preparation only gave a weak rose coloration; the purest sample from the La Motte Company gave a clear reaction. The iron content of the titanous solution can be easily determined potentiometrically by titration with potassium dichromate. The titration is best made by allowing the titanous solution, diluted with hydrochloric acid, to flow from a burette into the dichromate solution. The latter is reduced to the chromic stage, and at the same time any iron present in the titanous solution is oxidized to the ferric condition by the excess of dichromate. When all of the dichromate is reduced, a single drop of titanous solution causes the potential to fall from the high bichromate value to the very low titanous voltage.

If the titanous solution contains iron, ferric ion reacts after the dichromate has been reduced in the sense of the equation:

$$Fe^{+++} + Ti^{+++} \rightleftarrows Fe^{++} + Ti^{++++}.$$

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[126] I. M. Kolthoff and O. Tomicek, Rec. trav. chim., **43**, 775 (1924).

[127] E. Polidori, Z. anorg. Chem., **19**, 306 (1899).

In such a case there are therefore two breaks in potential, one after the reduction of dichromate, the other after the reduction of the ferric ions. The quantity of reagent used between the first and second jumps corresponds to the iron content of the solution. By this method Kolthoff and Tomicek (*loc. cit.*) found 2½ per cent of titanium, reckoned on the iron content, in a Kahlbaum preparation; 0 per cent after purification (Polidori); and 0.25 per cent in a La Motte preparation. The sample from the latter company also contained hydrogen sulphide.

*Stability of the Solution; Apparatus.*—The solution must be carefully protected from air. The strongly acid titanous solution attacks rubber. Care must therefore be taken that the solution never comes in contact with rubber during storage, or transfer to the burette. For this purpose Kolthoff and Tomicek used an apparatus of the same style as that of W. M. Thornton Jr., and E. Chapman.[128] The solution is placed in the storage bottle, B. The T-tube, C, ends above the liquid in B; one end of C is connected with the hydrogen generator, the other with the top of the burette, E. Oxidation of the titanous solution by air is thus prevented. The siphon tube, D, reaches to the bottom of the storage bottle and is joined to the burette by a small piece of rubber tube. The action of the solution on the rubber is prevented by bringing the ends of the two glass tubes into contact. The burette is filled by opening the tap, $A_1$. The tube, F, is sealed to the burette; its lower end is a very fine tip which delivers drops of 0.025 to 0.03 cc. each.

Upon opening stop-cock $A_2$ the titanous solution is brought into the titration vessel, I. The advantage of the bent tube, F, is that the burette is not warmed when a hot liquid is being titrated. The titration vessel, I, is closed with a six-hole rubber stopper. The end of F passes through the middle hole; the platinum electrode passes through another; through a third passes the siphon tube, filled with saturated potassium chloride solution, which leads to the normal calomel electrode vessel. Two other openings serve for the entrance and exit of carbon dioxide which is passed through the solution during titrations.

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[128] W. M. Thornton, Jr., and E. Chapman, J. Am. Chem. Soc., **43**, 91 (1921).

(The gas is purified by successive passage through titanous chloride solution and water.) The thermometer, T, fills the remaining hole in the stopper.

If care is exercised the solution is quite stable. W. M. Clark and B. Cohen (private communication) were able to keep a titanous solution unchanged in strength for several months. After fourteen days Kolthoff and Tomicek found a decrease in strength in their solution of 0.2 per cent. In general, it is recommended that the titer of the solution be determined every day.

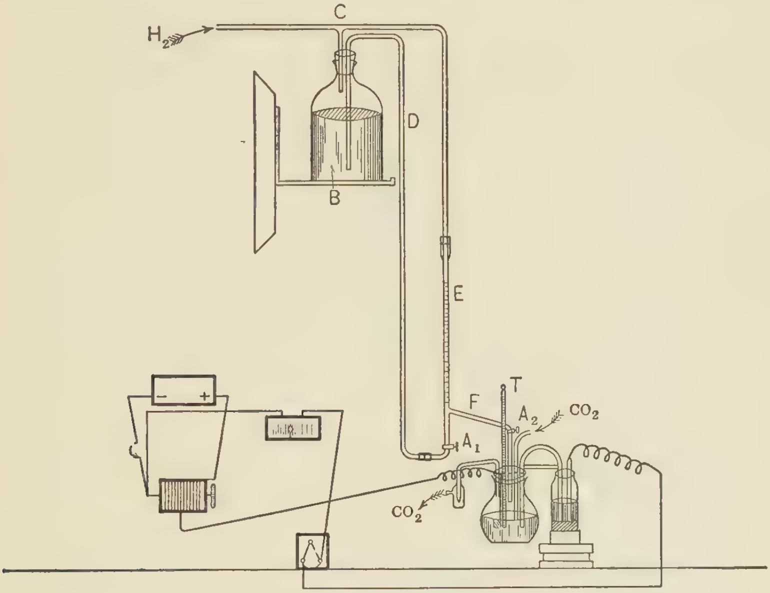

FIG. 45.—Apparatus for titrations in absence of air.

*Standardization of the Solution.*—According to W. S. Hendrixson,[129] iodate and bromate may be titrated very accurately with titanous solution. Hendrixson used titanous sulphate as a reagent with sulphuric acid solutions. Kolthoff and Tomicek failed to obtain good results when hydrochloric acid was used, because of the formation of volatile halogen compounds or of free halogen.

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[129] W. S. Hendrixson, J. Am. Chem. Soc., **45**, 2013 (1923). *Cf.* also Hendrixson and L. M. Verbeck, *ibid.*, **44**, 2382 (1922).

Pure potassium dichromate is a very suitable standard substance. Potassium ferricyanide and ferric ammonium alum may also be recommended. The former is obtained by rapid recrystallization from water and drying at 100°.[130] The ferric ammonium alum is obtained in the pure state by two recrystallizations from water. The salt is then dried in a desiccator at the aqueous tension given by saturated sugar and NaCl solution in contact with excess of the two solids (about 70 per cent humidity at room temperature).

The titrations are made in hydrochloric acid solution. When iron is absent there is only one break in potential; if it is present two breaks occur (*cf.* p. 289). With ferricyanide as a standard substance, only one break is found; it corresponds to the first in the titration of dichromate. The iron of the titanous solution is oxidized to the ferric state by the ferricyanide and is then removed as ferric ferrocyanide, which does not react—at least not rapidly—with an excess of titanous salt. If the titer is determined with ferric alum as standard substance, the break in potential naturally corresponds with the second break found in the dichromate titration.

E. Zintl and A. Rauch [131] recommend the use of a cupric salt solution for the standardization of titanous chloride solutions. In the opinion of the authors, the titration of cupric salt with this reducing agent does not give as accurate results as that of ferric salt or dichromate. Hence, the use of the latter standard substances is preferable.

*Application of Titanous Solution to Titration of Cations.*—Ferric Iron: This titration gives excellent results.[132] In the region of the end-point the last traces of iron are reduced slowly, so that one must wait a relatively long time for the potential to become steady. If the titration is made at 50°–60°, results are obtained much more rapidly and with as great accuracy as at room temperature. Inflection-potential, 0.100 volt (against N.C.E.). The titration may be made in the presence of a large excess of Rochelle salt. (This is of importance in the titration of dyestuffs.) The best results are obtained at 50°–90°. The value of the inflection-potential depends on the quantity of tartrate added: the more of the latter present, the lower its value. In a definite instance—with 10 g. Rochelle salt—it was − 0.300 volt. The titration does not give good results in the presence of fluoride.

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[130] I. M. Kolthoff, Pharm. Weekblad, **59**, 66 (1922).

[131] E. Zintl and A. Rauch, Z. Elektrochem., **31**, 428 (1925).

[132] I. M. Kolthoff and O. Tomicek, Rec. trav. chim., **43**, 798 (1924).

A. M. McMillan and W. C. Ferguson [133] have applied this potentiometric titration to the determination of iron in alloys.

*Copper.*—E. Zintl and H. Wattenberg [134] add an excess of titanous chloride solution to the cupric salt and then titrate with bromate (*cf.* p. 255). H. H. Willard and F. Fenwick [135] state in a brief note that the direct titration of copper with titanous sulphate gives satisfactory results. They give no further details.

Kolthoff and Tomicek (*loc. cit.*) found that too much reagent was used before the jump in potential occurred, the error being about 1 per cent. Inflection-potential, about − 0.30 volt (against N.C.E.) On the other hand, good results were obtained when the titration was made in the presence of sufficient potassium thiocyanate or iodide, whose cuprous salts are insoluble. The inflection-potential is higher in these cases: with thiocyanate present it is 0.00 volt (against N.C.E.), and with iodide, + 0.080 volt. In the presence of an excess of Rochelle salt too much reagent is used whether the solution is at room temperature or is warmed. (Error, 1–3 per cent.) If iodide is also present the results are satisfactory. Inflection-potential, − 0.60 volt. The titration may be carried out at 55°. When potassium thiocyanate is used instead of iodide there is an appreciable deviation from the theoretical values.

*Ferric and Cupric Salts.*—According to Kolthoff and Tomicek[136] ferric salts are reduced first. The jump in potential after the reduction of the iron is small, and good results are only obtained when the determination is made in acid solution at room temperature. Inflection-potential after iron reduction, 0.265 volt (against N.C.E.). If one titrates slowly to this potential, good results are obtained. After the reduction of the iron, 0.5 g. of potassium thiocyanate is added and the copper is determined as described above. If the ratio between the concentrations of ferric and cupric ions is unfavorable it is difficult to determine the first break in potential accurately.

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[133] A. M. McMillan and W. C. Ferguson, J. Soc. Chem. Ind., **44**, 141 (1925).

[134] E. Zintl and H. Wattenberg, Ber., **55**, 3366 (1922).

[135] H. H. Willard and F. Fenwick, J. Am. Chem. Soc., **45**, 933 (1923).

*Antimony.*—E. Zintl and H. Wattenberg[137] reduce quinquivalent antimony with an excess of titanous chloride. Kolthoff and Tomicek (*loc. cit.*, p. 802) apply the direct titration. The reduction goes extremely slowly at room temperature and the results are poor. On the other hand, the reduction is relatively rapid at 90–95°, and a determination may be made in half an hour. Inflection-potential, + 0.160 volt. The presence of arsenate has no disturbing effect on the direct titration of antimonate. When an arsenate solution is warmed for a long time with an excess of titanous solution, reduction takes place; finally arsenic itself is precipitated.

*Antimony and Iron.*—Although the oxidation-potential for quinquivalent antimony is but slightly different from that for ferric iron, we may make use of the slow reduction of antimony to estimate iron in its presence. The titration is made at room temperature, slowly near the end-point. After the potential break has been located the solution is warmed to 90°–95° and the quinquivalent antimony is reduced to the trivalent state.

The titration of *copper in the presence of quinquivalent antimony* is not so simple as the above. The cuprous salt which is formed acts as a catalyst in the reduction of the antimony. Useful results are obtained only when the titration is made in tartrate medium in the presence of potassium iodide.

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[136] I. M. Kolthoff and O. Tomicek, Rec. trav. chim., **43**, 812 (1924).

[137] E. Zintl and H. Wattenberg, Ber., **56**, 472 (1923).

*Uranium.*—Uranyl salts are reduced to quadrivalent uranous ions:

$$UO_2^{++} + 4H^+ + 2\ominus \rightleftarrows U^{++++} + 2H_2O.$$

According to Kolthoff and Tomicek (*loc. cit.*, p. 804) the results of the titration are satisfactory for hydrochloric acid solutions. If the work is done at room temperature, a long time elapses after each addition of reagent before the potential is constant; if the titration is made with the solution at 55°–60°, good values are obtained relatively rapidly. The more acid the solution, the higher is the potential during the titration; the inflection-potential depends upon the acidity. In 10 per cent hydrochloric acid it was + 0.040 volt; in 1.25 per cent HCl, – 0.130 volt (against N.C.E.). Excellent results are obtained in the presence of an excess of tartrate; it is therefore recommended that the titration be made with much Rochelle salt present (accuracy, 0.2 per cent). Inflection-potential, – 0.380 volt; temperature, 75°. Particular care must be exercised in shielding the solution from air, because uranous salts are easily oxidized.

*Ferric* and *uranyl* salts may be easily determined in the presence of each other (Kolthoff and Tomicek, *loc. cit.*, p. 814). The ferric salt is first reduced. The determination may be made in hydrochloric acid solution. After the reduction of the iron it is well to add an excess of Rochelle salt. The first inflection-potential (completion of reduction ferric to ferrous ion) is 0.240 volt. The results are accurate.

*Bismuth.*—In weakly acid solution bismuth ions are reduced to metal by titanous chloride. E. Zintl and A. Rauch [138] have applied this fact in the potentiometric titration of bismuth salts. The reduction goes very slowly at room temperature; at 80° the potential soon becomes constant. Titanic acid also separates in the warm, weakly acid solution at the same time as the finely divided bismuth. Since this titanic acid includes some bismuth salt, Zintl and Rauch add tartaric acid which prevents the precipitation of titanic acid. The bismuth precipitates as a dark powder which is deposited in flocs on the platinum electrode during the titration. Under these conditions the results are irregular, often differing by several per cent from the correct value. Hence care must be taken that the electrode is not entirely covered with bismuth. In this way accurate results are obtained. The electrode must be ignited after a few successive titrations. It must be cleaned in a dichromate-sulphuric acid bath before every titration. The sharpness of the potential break is dependent upon the acid concentration. The free hydrochloric acid content may not exceed 0.5 per cent. The bismuth is kept in solution by the addition of sufficient tartaric acid and sodium chloride. Carbon dioxide is passed through the solution during the titration. Inflection-potential, 0.140 volt (against N.C.E.). Maximum error, 1 drop 0.1 N $TiCl_3$, which equals 0.2 mg. bismuth.

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[138] E. Zintl and A. Rauch, Z. anorg. Chem., **39**, 397 (1924).

Nitrate has a disturbing effect. In the presence of acetic acid—acetate buffer, the jump in potential after the complete precipitation of the bismuth is much greater than in dilute hydrochloric acid solution. Enough acetate must be added to bind all free mineral acid. Sodium chloride is added if the solution becomes turbid. Tartaric acid may also be added. The best results are found when the solution is warm during titration (80°). Inflection-potential, − 0.340 volt (against N.C.E.). When Müller's method is followed the titration gives a good result in two minutes' time. Nitrate must be absent. The authors suggest that the titration will also be successful in the presence of a large excess of Rochelle salt. This bismuth titration, as described by Zintl and Rauch, is of special advantage when the solution contains lead. When the titration is made with dilute hydrochloric acid or acetate medium (great excess of ammonium acetate), bismuth alone is precipitated.

In a further study of the subject, E. Zintl and A. Rauch [139] give the details of the determination of bismuth in the presence of other metals. It may be concluded from their results that the titration does not give theoretical results in either hydrochloric or acetic acid media. A 1.2 per cent excess of titanous chloride is required. According to Zintl and Rauch, the deviation is constant and is independent of the nature of the solution. In the presence of cupric copper, or of iron salts, the excess is diminished to 0.6 per cent. The authors believe that a further systematic study of this method of titration is necessary.

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[139] E. Zintl and A. Rauch, Z. anorg. allgem. Chem., **146**, 291 (1925).

A jump in potential occurs at the completion of the reduction of ferric salts, after which the bismuth is precipitated. Cupric copper, if present, is reduced to the cuprous condition before the beginning of the reduction of bismuth to metal. A jump in potential occurs at the end of each of these processes. Finally, cuprous copper is reduced to the metallic condition. Zintl and Rauch recommend the addition of as much as 5 to 10 per cent of sodium chloride in order to prevent the simultaneous precipitation of metallic bismuth and copper. The sodium chloride forms a complex with the cuprous chloride. The titration must be made in hydrochloric acid solution if iron and copper salts are present. In this instance the determination is not possible in the presence of acetic acid and acetate. The titration must be carried out in acetate medium if stannic tin is present. If the solution contains only hydrochloric acid and chlorides, cadmium and arsenic do not interfere. The presence of antimony, however, makes the bismuth determination impossible.

*Gold.*—According to E. Zintl and A. Rauch,[140] the gold of an auric salt solution is reduced to the aurous form and then to the metallic state by warm titanous chloride solution in a hydrochloric acid medium. Before the beginning of the titration they add several drops of potassium bromate in order to be sure that all of the gold is present in the auric form. In the titration with the reducing agent, the first jump in potential occurs at the point where all of the bromate is reduced, the second after quantitative reduction of the gold to the metallic state. The first inflection-potential lies at 0.760 volt, the second at 0.240 volt against the saturated calomel electrode. Even very small amounts of gold—as little as a few milligrams—may be determined with great accuracy (about 1 per cent). Mercury, tin, lead and bismuth do not interfere.

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[140] E. Zintl and A. Rauch, Z. Elektrochem., **31**, 428 (1925).

In the presence of cupric solution the gold is first reduced, and then cupric reduced to cuprous ion.

Ferric iron and gold establish an equilibrium in hydrochloric acid solution. The ferric ions are bound in a complex, however, by the addition of phosphoric acid, and the titration of gold is then possible.

*Titration of Anions.—Permanganate.*—The titration of this oxidant with titanous sulphate gives accurate results, according to Hendrixson and Verbeck.[141] It can not be titrated with titanous chloride because hydrochloric acid interferes.

*Dichromate.*—The titration yields good results; toward the end of the reduction the potential changes relatively slowly and it is necessary to wait a few minutes until it becomes constant. Kolthoff and Tomicek (*loc. cit.*, p. 784) state that the jump is very great, being 600 millivolts for 0.025 cc. of 0.1 N reagent. At 50°–60° the potential becomes constant more rapidly, so that it is advantageous to work at the higher temperature. Inflection-potential (with iron-free titanous chloride), + 0.300 volt. This value, however, changes with the acidity of the solution.

*Dichromate and Ferric Iron.*—The dichromate is first reduced and then the iron. If both are present in equivalent concentrations the inflection-potential is + 0.590 volt; if the ratio is 1 : 2.5, the voltage is + 0.610; at 1 : 100 it is .650 volt. In the latter case dichromate may still be determined in the presence of iron with an accuracy of 0.2 per cent (Kolthoff and Tomicek, *loc. cit.*, p. 809). In general, it is not advisable to titrate to a definite inflection-potential because its value is somewhat dependent upon the acidity of the solution.

*Ferricyanide.*—W. S. Hendrixson [142] obtained good results in the titration of ferricyanide with titanous sulphate. When using titanous chloride, Kolthoff and Tomicek (*loc. cit.*, p. 785) also found accurate values, although the break in potential is smaller than in the dichromate titration. A brown precipitate of titanic ferrocyanide is produced during the titration. The potential rapidly assumes constant values after each addition of reagent; within wide limits the acidity of the solution is without influence on the result. Inflection-potential, about + 0.200 volt (against N.C.E.). The titration must be made at room temperature since the ferricyanide is decomposed in warm acid solution. The jump in potential is much greater when the titration is in tartrate medium; the liquid remains clear during the titration. The results are accurate under these conditions.

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[141] W. S. Hendrixson and L. M. Verbeck, J. Am. Chem. Soc., **44**, 2382 (1922).

[142] W. S. Hendrixson, J. Am. Chem. Soc., **45**, 2013 (1923).

*Dichromate and Ferricyanide.*—The dichromate is reduced before the ferricyanide. Kolthoff and Tomicek (*loc. cit.*, p. 811) obtained good results when the solution contained at least 7 per cent of hydrochloric acid. The first inflection-potential, corresponding to the end of the dichromate reduction, lies at + 0.850 volt (against N.C.E.); the second, corresponding to reduction of ferricyanide, is at 0.220 volt.

*Vanadate.*—Vanadate is reduced to quadrivalent vanadyl salt:

$$VO_4^{---} + 6H^+ + Ti^{+++} \rightleftarrows VO^{++} + Ti^{++++} + 3H_2O.$$

During the titration the potential alters very regularly and soon becomes constant after additions of reagent. The reflection-potential is at + 0.280 volt when the titanium solution is free from iron, whereas if iron is present it lies at + 0.540 volt. There is no advantage in carrying out the titration in hot solution. The first jump in potential occurs when quadrivalent vanadium salt has been formed.

Now vanadyl ion may be still further reduced, viz., to trivalent vanadium; according to Th. F. Rutter[143] the normal potential of the system $\frac{[V^{IV}]}{[V^{III}]}$ is + 0.312 volt (referred to the normal hydrogen electrode).

Kolthoff and Tomicek found that more than the theoretical amount of reagent was used in acid solution. Better results were obtained in tartrate medium. The titration, with a

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[143] R. Peters, Z. physik. Chem., **26**, 193 (1898); Th. F. Rutter, Z. anorg. Chem., **52**, 368 (1907); M. Hofer and F. Jacob, Ber., **41**, 3187 (1908).

Rochelle salt solution, may be made more quickly at 50°–60° than at room temperature. Inflection-potential, about − 0.120 volt (N.C.E.). When the titanous solution contains iron, three potential breaks are found in the titration of the vanadate solution. The vanadate is first titrated in acid solution; the tartrate must not be present at the start because vanadate has an oxidizing action on the tartrate. After the first break in potential has been reached the Rochelle salt is added and the titration is continued at 50°–60° to the second break.

*Vanadate, Dichromate, and Ferric Iron.*—When a mixture of these three substances is titrated with a titanous solution the vanadate and dichromate are first reduced simultaneously, after which the reduction of the iron begins. If the ratio of the components of the mixture is not unfavorable, all three substances may be determined by one titration. It is first carried to the initial potential jump, where dichromate has been completely reduced to chromic salts, and the vanadate to quadrivalent vanadium; the ferric salt is then reduced, and then, after addition of Rochelle salt, the quadrivalent vanadium is reduced to the trivalent stage. By subtracting the amount of reagent used between the second and third inflections ($V^{IV} \rightarrow V^{III}$), from that required up to the first, we have the number of cubic centimeters of reagent which were required for the reduction of the dichromate. Accurate results are obtained in the above-described manner.

*Iodate.*—The titration of iodate with titanous sulphate gives good results. W. S. Hendrixson [144] found the first break in potential after complete reduction of iodate to iodine. On continued addition of reagent a second break is found, after more than enough reagent to reduce the iodine has been added. Kolthoff and Tomicek (*loc. cit.*, p. 791) confirmed the noteworthy fact that iodine reacts slowly with titanous solution. They found that the titration goes smoothly in presence of cupric ions. They stated that three breaks in potential occur when titrating with titanous chloride solution. The first corresponds to complete reduction of iodic acid to hypo-iodous acid,

[144] W. S. Hendrixson, J. Am. Chem. Soc., **45**, 2013 (1923).

the second occurs after reduction to iodine, and the third when iodine has been reduced to iodide. The titration of iodate with titanous solutions is of little analytical significance.

*Bromate.*—According to Hendrixson (*loc. cit.*), the bromate titration may be carried out more satisfactorily in hydrochloric than in sulphuric acid solution. He used a mercury seal so that no bromine could escape during titration. A large change in potential is found when the bromate has been reduced to bromide.

*Chlorate.*—The potential curve has about the same form as in the bromate titration, with the difference that the potential lies somewhat higher during the titration. The break in potential upon complete reduction to chloride is very large, being about 1 volt for 0.1 cc. of 0.1 N solution.

*Molybdate.*—The reduction of molybdic acid to quinquivalent molybdenum by trivalent titanium was observed by Knecht and Hibbert. They did not base a volumetric method for molybdenum upon this fact. H. H. Willard and F. Fenwick [145] found that the reduction was sufficiently rapid for the application of the potentiometric method. They used the polarized bimetallic system. They found that ordinarily the maximum was perfectly definite with slow addition of reagent near the end-point. Equilibrium is maintained in this way; otherwise an irregular and transient decrease in E.M.F. may result before the reaction is quite complete. They state that it is safest to add several drops more of titanous solution after the supposed end-point is reached, to make sure that the potential decrease is permanent and is becoming larger. The rate of reduction is not ideally rapid. For this reason Willard and Fenwick suggest that a better end-point would be obtained with the usual monometallic electrode system. They found that more reagent was used than the theoretical quantity for reduction from molybdic acid to quinquivalent molybdenum; under certain conditions the error may be 2 to 3 per cent.

I. M. Kolthoff and O. Tomicek [146] made a careful investigation of the molybdate titration, using the monometallic system, and were unable to confirm the above statement. In agreement with Willard and Fenwick, they found that the solution must be warm when titrated. The most suitable temperature is 75°–80°. They also confirmed Willard and Fenwick's conclusion that the solution must be fairly acid; a concentration of 5–10 per cent of hydrochloric acid is advisable. When a determination is made under these conditions it is found that the first drops of titanous chloride color the solution brown; it then becomes yellowish brown, and finally a muddy brown. Kolthoff and Tomicek obtained excellent results even when the quantity of molybdenum was small. Inflection-potential, about + 0.01 volt (against N.C.E.). If the titanous chloride contains iron, good results are obtained provided that the titer is found with ferric alum as a standard.

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[145] H. H. Willard and F. Fenwick, J. Am. Chem. Soc., **45**, 928 (1923).

[146] I. M. Kolthoff and O. Tomicek, Rec. trav. chim., **43**, 788 (1924).

Willard and Fenwick applied the method to the determination of molybdenum in ammonium phospho-molybdate. Kolthoff and Tomicek found that phosphoric acid had a disturbing action; too little reagent was required. The color of the liquid is different from that observed when phosphoric acid is absent; it rapidly becomes blue during titration, and finally becomes turbid. It is an interesting fact that tungstate does not interfere with the molybdate titration (Willard and Fenwick).

*Selenite.*—Monnier [147] and also Moser [148] observed the fact that selenious acid is reduced to metal by titanous chloride. H. H. Willard and F. Fenwick [149] titrated selenious acid with titanous sulphate potentiometrically, using the bimetallic electrode system:

$$SeO_3^{=} + 6H^+ + 4Ti^{+++} \rightleftarrows Se + 4Ti^{++++} + 3H_2O.$$

They found that the reaction takes place quantitatively as shown in the equation when the solution contains 25 to 75 cc. of concentrated sulphuric acid per 100 cc. of solution. With small acidity their results were not good. The liquid was saturated with sodium chloride, which aids in the coagulation of the selenium during the titration, thus enabling the end-point to be determined accurately.

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[147] M. A. Monnier, Ann. chim. anal. appl., **20**, 1 (1915).

[148] L. Moser and W. Prinz, Z. analyt. Chem., **57**, 300 (1918).

[149] H. H. Willard and F. Fenwick, J. Am. Chem. Soc., **45**, 933 (1923).

Kolthoff and Tomicek[150] used the monometallic system and found that the potential assumed a steady value very slowly at room temperature; on the other hand, at 50°–60° the determination may be carried out fairly rapidly. They confirmed the conclusions of Willard and Fenwick with regard to the effect of acidity and presence of sodium chloride. The inflection-potential is dependent on the acidity, being higher with larger acid content of the liquid. In a liquid containing 6 per cent of hydrochloric acid it is + 0.150 volt; with 15 per cent of acid, + 0.190 volt; with 19 per cent HCl, + 0.230 volt. Accuracy is 0.1–0.2 per cent. It is not essential to carry out the titration in a strongly acid medium; good results are obtained in the presence of a large excess of Rochelle salt if one titrates at 55°. The inflection-potential lies much lower than in acid medium; thus in the titration of a mixture of 25 cc. of 0.1 N selenious acid, 25 cc. of 30 per cent Rochelle salt and 50 cc. of water, it was – 0.300 volt (against N.C.E.)

According to Willard and Fenwick (*loc. cit.*), one of the most surprising and interesting things in connection with the selenium determination is the fact that the volume of titanium solution used in the titration of mixtures of selenium and ferric iron is the same as that for selenium alone, although ferrous iron is formed during the precipitation. In opposition to this, Kolthoff and Tomicek found that ferric iron was reduced simultaneously and quantitatively and that there was one potential break at the completion of the reduction of both substances. According to Willard and Fenwick, tellurium, even in large quantities, does not interfere with the titration of selenium although it seems to affect the character of the end-point. "The fall in potential as the end-point is passed does not always occur, but the rise is fully as sharp as in the absence of these substances."

When cupric salts are present the potentiometric titration gives two end-points, according to Willard and Fenwick. The first occurs when selenium is completely precipitated, the second at the conclusion of the reduction of the copper. "Towards the end of the first reaction the voltage starts to rise slightly. There is a long, distinct upward swing that marks the end-point, followed usually by continued rise. The copper end-point is a second sharp rise." Kolthoff and Tomicek, however, found when using the monometallic system that the cupric salt was reduced simultaneously with the selenious acid.

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[150] I. M. Kolthoff and O. Tomicek, Rec. tiav. chim., **43**, 794 (1924).

*Nitrite; Nitrate; Per Salts.*—Kolthoff and Tomicek were not successful in determining these substances by direct titration with titanous solution. Even the reaction between titanous chloride and hydrogen peroxide takes place very slowly.

*Dyestuffs; Nitro Compounds.*—The direct titration of dyestuffs and nitro compounds with titanous chloride has not yet been studied. The authors suggest that these titrations will be possible under the proper conditions.[151] Thus Kolthoff and Tomicek (unpublished studies) found that the direct titration of methylene blue was possible in the presence of Rochelle salt. There was a sharp break in potential at the end-point.

Kolthoff and Robinson (unpublished investigation) titrate nitro compounds in a very simple way. As Kolthoff showed (p. 287), the reduction-potential increases regularly with decreasing hydrogen-ion concentration; reduction is therefore complete much sooner at low acidities than at larger hydrogen-ion concentrations. Kolthoff and Robinson apply this principle in the estimation of nitro compounds. Thirty cubic centimeters of 20 per cent sodium citrate (tertiary salt) are added to the solution to be titrated, and then carbon dioxide is passed through. After three minutes the air is removed, and titanous solution is added slowly until the solution is distinctly dark violet colored. When this point has been reached there is only a slight excess of titanous salt which is titrated back with ferric alum solution of known strength. The titanous chloride may be standardized in citrate medium with a pure ferric alum solution. In all of the cases investigated, the theoretical values were found. Boiling is unnecessary as the reduction takes place quickly enough at room temperature. A direct titration of the nitro compound under these conditions can not be recommended, because the reduction of the last traces of the nitro compound at the equivalence-point goes very slowly and it takes a long time (forty minutes) to finish the titration.

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[151] The indirect potentiometric titration of aromatic nitro compounds has been studied by F. L. English, J. Ind. Eng. Chem., **12**, 994 (1920); of azo coloring matters by D. O. Jones and H. R. Lee, J. Ind. Eng. Chem., **14**, 46 (1922); of triphenyl methane and azo compounds by W. S. Calcott and F. L. English, J. Ind. Eng. Chem., **15**, 1042 (1923).

In citrate medium there is no danger whatever of chlorination of the nitro product. The method therefore has distinct advantages over the usual procedures applied by organic chemists.

When we are dealing with volatile nitro bodies the carbon dioxide is only passed through the citrate solution. When the latter is air-free, the nitro body is added and the passage of carbon dioxide is stopped. After thorough stirring the titanium chloride is added and when an excess is present the carbon dioxide stream is again passed through. In working with nitro benzene and other volatile nitro compounds, Kolthoff and Robinson obtained correct results.

As a matter of fact, the method may also be applied to the determination of other organic compounds that are reducible by titanous chloride (nitroso compounds, dyestuffs, etc.).

In this connection, mention should be made of the important work of W. M. Clark and B. Cohen [152] on the reduction-potentials of indigo sulphonates and indigo phenols.

We may also anticipate that a direct titration of quinones will be possible.

**13. Reduction with Stannous Salts.**—The direct potentiometric titration of ferric iron with stannous chloride gives unsatisfactory results, according to H. R. Adam.[153] He adds an excess of reducing agent to the hot ferric solution and titrates back with dichromate or iodine (*cf.* p. 251). The presence of titanium in the solution does not affect the reduction of ferric ion by stannous chloride.

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[152] W. M. Clark and B. Cohen, U. S. Public Health Reports, **38**, 443, 666, 933, 1669 (1923); **39**, 381, 804 (1924).

[153] H. R. Adam. I. S. African Chem. Inst., 8, 7 (1925); through Chem. Abstracts, **19**, 1832 (1925).

Apparently other possibilities of the use of stannous salts as reductants in potentiometric titrations have not been studied.

## ADDENDUM

### REDUCTION WITH FERROCYANIDE

**The Reaction between Ferrocyanide and the Halogens.**—Carlos del Fresno[154] found a large jump in potential at the equivalence-point of the reaction between chlorine and ferrocyanide. When bromine is titrated in the same manner the jump is smaller, and with iodine only a very slight change in potential is found at the equivalence-point.

If the N.C.E. is used as standard half cell the inflection-potentials found by del Fresno are:

| Reaction | Starting with Halogen | Starting with Ferrocyanide |
|---|---|---|
| | Volt | Volt |
| $Cl_2 + 2Fe(CN)_6^{\stackrel{=}{=}} \rightleftarrows 2Cl^- + 2Fe(CN)_6^{\equiv}$ ...... | 0.656 | 0.626 |
| $Br_2 + 2Fe(CN)_6^{\stackrel{=}{=}} \rightleftarrows 2Br^- + 2Fe(CN)_6^{\equiv}$ ...... | 0.549 | 0.554 |
| $I_2 + 2Fe(CN)_6^{\stackrel{=}{=}} \rightleftarrows 2I^- + 2Fe(CN)_6^{\equiv}$ ...... | 0.263 | 0.251 |

The first two titrations have no analytical significance because of the volatility of bromine and chlorine. The potential break in the titration with or of iodine is too small, in the authors' opinion, to give accurate results. Del Fresno remarks, moreover, that the jump does not occur exactly at the equivalence-point.

### TITRATION WITH SODIUM NITRITE

**Application of the Potentiometric Method to Diazotation, and the Quantitative Determination of Amines.**—When the solution of an aromatic amine is diazotized free nitrous acid is formed at the completion of the reaction. A solution of nitrous acid, in contact with a platinum electrode, gives a definite potential. E. Müller and E. Dachselt [155] have found that there is a jump in potential at the equivalence-point of the titration of the acid solution of an aromatic amine with sodium nitrite.

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[154] Carlos del Fresno, Z. Elektrochem., **31**, 617 (1925).

In the titration of aniline the reaction is:

$$C_6H_5NH_2HCl + NaNO_2 + HCl \rightleftarrows C_6H_5N_2Cl + NaCl + 2H_2O.$$

The partial reactions that determine the potential are not known.

The potential requires a long time to become steady during the titration. Therefore it is necessary to wait five minutes or more after each addition of reagent. The liquid must be stirred vigorously to obtain regular E.M.F. readings. The potential reaches a maximum at the equivalence-point, falling upon further addition of nitrite. Müller and Dachselt ascribe this behavior to the nitrous acid. If dilute hydrochloric acid is added to a nitrite solution the potential falls with increasing nitrous acid concentration.

The " Müller system " is recommended as practically convenient. When the N.C.E. is used as reference electrode a potential of 0.58 volt is opposed to the reaction cell, a potential divider being used to secure the proper voltage. The end-point is reached when the zero-point instrument (galvanometer or capillary electrometer) gives no deflection. Equilibrium is reached very slowly in the neighborhood of the end-point, and it is necessary to wait some time after a zero reading is obtained to be sure that the potential is constant. If this is not the case, nitrite is added drop by drop until the galvanometer reading is constant at zero. At this point the liquid does not give a reaction with iodide-starch paper; the next drop does react with the paper. Müller and Dachselt studied the titration of aniline (inflection-potential + 0.59 volt), xylidene (+ 0.56 volt), toluidene (+ 0.58 volt), and amino azo benzene disulphonic acid (+ 0.54 volt).

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[155] E. Müller and E. Dachselt, Z. Elektrochem., **31**, 662 (1925).

For technical purposes it is still easier to use the Pinkhof system. Müller and Dachselt therefore recommend a platinum electrode dipped into an acid solution of the same concentration as that of the liquid to be titrated, and containing 1.92 per cent of sodium nitrite, as an auxiliary electrode. The dip electrode described by E. Müller [156] also gives good results.

Attempts were made to accelerate the reaction by using higher temperatures. Side reactions occur, causing errors: 3 per cent at 60°; 0.5 per cent at 30°. At 20° or below the results are very accurate. Hence it is not necessary to cool in ice during the diazotization. Müller and Dachselt did not study the effect of acid concentration on the inflection-potential.

Care is necessary in the application of the above method in the opinion of Kolthoff, who had attempted to apply the reaction in the titration of dilute solutions of primary amines before the appearance of the paper by Müller and Dachselt. He did not succeed in obtaining accurate results. No large jump in potential could be obtained even when the solutions were cooled in ice. Müller and Dachselt applied their method in concentrated solutions. For instance, they titrated a solution of 2.5 g. of aniline in 8 g. conc. hydrochloric acid, and 40 cc. of water, with a solution containing 196.2 g. sodium nitrite per liter.

A more systematic study of the titration would be desirable.

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[156] E. Müller, Z. Elektrochem., **30**, 422 (1924).

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# TABLES

## TABLE I

### STANDARD VALUES FOR CALOMEL ELECTRODES (REFERRED TO THE NORMAL HYDROGEN ELECTRODE)

| Electrode | E.M.F. |
|---|---|
| 0.1 N Calomel Electrode | $0.3380 + 0.00006(t-18)$ |
| 1 N Calomel Electrode | $0.2864 + 0.00024(t-18)$ |
| 3.5 N Calomel Electrode | $0.2549 + 0.00039(t-18)$ |
| Saturated Calomel Electrode | $0.2504 + 0.00065(t-18)$ |

Value of 0.0001983T in the formula:

$$E = \epsilon_0 - 0.0001983T \log c = \epsilon_0 - A \log c.$$

$$A = 0.0577 + 0.0002(t - 18)$$

between $t = 10°$ and $30°$.

## TABLE II

### NORMAL POTENTIALS

The values are taken from No. 8 der Abh. der Deutschen Bunsengesellschaft, 1915. The potentials are referred to the normal hydrogen electrode.

| Electrode Reaction | Normal Potential |
|---|---|
| $Li \rightleftarrows Li^+ + \ominus$ | $-3.02$ Volts |
| $K \rightleftarrows K^+ + \ominus$ | $-2.92$ |
| $Ba \rightleftarrows Ba^{++} + 2\ominus$ | $-2.8$ |
| $Na \rightleftarrows Na^+ + \ominus$ | $-2.71$ |
| $Sr \rightleftarrows Sr^{++} + 2\ominus$ | $-2.7$ |
| $Ca \rightleftarrows Ca^{++} + 2\ominus$ | $-2.5$ |
| $Mg \rightleftarrows Mg^{++} + 2\ominus$ | $-1.55$ |
| $Zn + 3OH^- \rightleftarrows ZnO_2H^- + H_2O + 2\ominus$ | $-1.18$ |
| $Mn \rightleftarrows Mn^{++} + 2\ominus$ | $-1$ |
| $Cu + HS^- + OH^- \rightleftarrows CuS_{solid} + H_2O + 2\ominus$ | $-0.89$ |
| $H_2 + 2OH^- \rightleftarrows 2H_2O + 2\ominus$ | $-0.82$ |
| $Hg + HS^- + OH^- \rightleftarrows HgS_{solid} + H_2O + 2\ominus$ | $-0.77$ |
| $Zn \rightleftarrows Zn^{++} + 2\ominus$ | $-0.76$ |
| $2Ag + HS^- + OH^- \rightleftarrows Ag_2S_{solid} + H_2O + 2\ominus$ | $-0.67$ |
| $Cr \rightleftarrows Cr^{++} + 2\ominus$ | $-0.6$ |
| $Pb + HS^- + OH^- \rightleftarrows PbS_{solid} + H_2O + 2\ominus$ | $-0.56$ |
| $Pb + 2OH^- \rightleftarrows PbO_{solid} + H_2O + 2\ominus$ | $-0.56$ |
| $2NH_{3\ dissolved} + H_2 \rightleftarrows 2NH_4^+ + 2\ominus$ | $-0.55$ |
| $S^{=} \rightleftarrows S_{solid} + 2\ominus$ | $-0.55$ |
| $HS^- + OH^- \rightleftarrows S_{solid} + H_2O + 2\ominus$ | $-0.51$ |
| $Ag + 2CN^- \rightleftarrows Ag(CN)_2^- + \ominus$ | $-0.51$ |
| $Fe \rightleftarrows Fe^{++} + 2\ominus$ | $-0.43$ |
| $Cd \rightleftarrows Cd^{++} + 2\ominus$ | $-0.40$ |
| $2Cu + 2OH^- \rightleftarrows Cu_2O_{solid} + H_2O + 2\ominus$ | $-0.35$ |
| $Pb + SO_4^{=} \rightleftarrows PbSO_{4\ solid} + 2\ominus$ | $-0.34$ |

TABLE II—*Continued*

| Electrode Reaction | Normal Potential |
|---|---|
| $Tl \rightleftarrows Tl^{+} + \ominus$ | − 0.33 Volts |
| $Pb + 2I^{-} \rightleftarrows PbI_{2\,\mathrm{solid}} + 2\ominus$ | − 0.31 |
| $Co \rightleftarrows Co^{++} + 2\ominus$ | − 0.29 |
| $Pb + 2Br^{-} \rightleftarrows PbBr_{2\,\mathrm{solid}} + 2\ominus$ | − 0.27 |
| $Pb + 2Cl^{-} \rightleftarrows PbCl_2 + 2\ominus$ | − 0.26 |
| $Ni \rightleftarrows Ni^{++} + 2\ominus$ | − 0.22 |
| $Cu + I^{-} \rightleftarrows CuI_{\mathrm{solid}} + \ominus$ | − 0.17 |
| $Ag + I^{-} \rightleftarrows AgI_{\mathrm{solid}} + \ominus$ | − 0.14 |
| $Pb \rightleftarrows Pb^{++} + 2\ominus$ | − 0.12 |
| $Sn \rightleftarrows Sn^{++} + 2\ominus$ | − 0.10 |
| $Fe \rightleftarrows Fe^{+++} + 3\ominus$ | − 0.04 |
| $2Hg + 2I^{-} \rightleftarrows Hg_2I_{2\,\mathrm{solid}} + 2\ominus$ | − 0.03 |
| $H_2 \rightleftarrows 2H^{+} + 2\ominus$ | 0.00 |
| $Sn \rightleftarrows Sn^{++++} + 4\ominus$ | + 0.05 |
| $Ag + Br^{-} \rightleftarrows AgBr_{\mathrm{solid}} + \ominus$ | + 0.08 |
| $Hg + 2OH^{-} \rightleftarrows HgO_{\mathrm{solid}} + H_2O + 2\ominus$ | + 0.11 |
| $Cu + Cl^{-} \rightleftarrows CuCl_{\mathrm{solid}} + \ominus$ | + 0.13 |
| $Ag + Cl^{-} \rightleftarrows AgCl_{\mathrm{solid}} + \ominus$ | + 0.22 |
| $2Hg + 2Cl^{-} \rightleftarrows Hg_2Cl_{2\,\mathrm{solid}} + 2\ominus$ | + 0.275 |
| $Cu \rightleftarrows Cu^{++} + 2\ominus$ | + 0.34 |
| $2Ag + 2OH^{-} \rightleftarrows Ag_2O_{\mathrm{solid}} + H_2O + 2\ominus$ | + 0.35 |
| $Fe(CN)_6^{\equiv} \rightleftarrows Fe(CN)_6^{=} + \ominus$ | + 0.40 |
| $4OH^{-} \rightleftarrows O_2 + 2H_2O + 4\ominus$ | + 0.41 |
| $Co \rightleftarrows Co^{+++} + 3\ominus$ | + 0.42 |
| $Cu \rightleftarrows Cu^{+} + \ominus$ | + 0.52 |
| $2I^{-} \rightleftarrows I_2 + 2\ominus$ | + 0.54 |
| $2Hg + SO_4^{=} \rightleftarrows Hg_2SO_4 + 2\ominus$ | + 0.62 |
| $Tl \rightleftarrows Tl^{+++} + 3\ominus$ | + 0.72 |
| $2Hg \rightleftarrows Hg_2^{++} + 2\ominus$ | + 0.75 |
| $Ag \rightleftarrows Ag^{+} + \ominus$ | + 0.80 |
| $Hg \rightleftarrows Hg^{++} + 2\ominus$ | + 0.86 |
| $NO + H_2O \rightleftarrows NO_3^{-} + 4H^{+} + 3\ominus$ | + 0.95 |
| $2OH^{-} \rightleftarrows H_2O_2 + 2\ominus$ | + 1 |
| $2Br^{-} \rightleftarrows Br_2 + 2\ominus$ | + 1.08 |
| $2H_2O \rightleftarrows O_{2\,\mathrm{gas}} + 4H^{+} + 4\ominus$ | + 1.23 |
| $Au \rightleftarrows Au^{+++} + 3\ominus$ | + 1.3 |
| $Cr^{+++} + 4H_2O \rightleftarrows HCrO_4^{-} + 7H^{+} + 3\ominus$ | + 1.3 |
| $Mn^{++} + 2H_2O \rightleftarrows MnO_{2\,\mathrm{solid}} + 4H^{+} + 2\ominus$ | + 1.35 |
| $2Cl^{-} \rightleftarrows Cl_2 + 2\ominus$ | + 1.36 |
| $Cl^{-} + 3H_2O \rightleftarrows ClO_3^{-} + 6H^{+} + 6\ominus$ | + 1.44 |
| $Pb^{++} + 2H_2O \rightleftarrows PbO_{2\,\mathrm{solid}} + 4H^{+} + 2\ominus$ | + 1.44 |
| $Au \rightleftarrows Au^{+} + \ominus$ | + 1.5 |
| $MnO_{2\,\mathrm{solid}} + 2H_2O \rightleftarrows MnO_4^{-} + 4H^{+} + 3\ominus$ | + 1.63 |
| $PbSO_{4\,\mathrm{solid}} + 2H_2O \rightleftarrows PbO_2 + 4H^{+} + SO_4^{=} + 2\ominus$ | + 1.66 |
| $O + H_2O \rightleftarrows O_2 + 2H^{+} + 2\ominus$ | + 1.9 |
| $2F^{-} \rightleftarrows F_{2\,\mathrm{gas}} + 2\ominus$ | + 1.9 |

## TABLE III

### Ionization Constant of Water at Various Temperatures

| Temperature | $K_w$ | $pK_w$ |
|---|---|---|
| 0° | $0.1\times10^{-14}$ | 14.92 |
| 10 | $0.3\times10^{-14}$ | 14.52 |
| 18 | $0.7\times10^{-14}$ | 14.16 |
| 25 | $1.2\times10^{-14}$ | 13.92 |
| 30 | $1.8\times10^{-14}$ | 13.75 |
| 50 | $8\times10^{-14}$ | 13.10 |
| 60 | $12.6\times10^{-14}$ | 12.90 |
| 70 | $21.2\times10^{-14}$ | 12.67 |
| 80 | $35\times10^{-14}$ | 12.46 |
| 90 | $53\times10^{-14}$ | 12.28 |
| 100 | $73\times10^{-14}$ | 12.14 |

## TABLE IV

### Dissociation Constants of Some Acids and Bases

| Acid | $K_a$ | $p_K (= -\log K_a)$ |
|---|---|---|
| Inorganic Acids | | |
| Arsenious oxide | $6\times10^{-10}$ | 9.22 |
| Arsenic acid, first step | $5\times10^{-3}$ | 2.30 |
| Boric acid | $6.6\times10^{-10}$ | 9.18 |
| Carbonic acid, first step | $3.04\times10^{-7}$ | 6.52 |
| second step | $6\times10^{-11}$ | 10.22 |
| Phosphoric acid, first step | $1.1\times10^{-2}$ | 1.96 |
| second step | $1.95\times10^{-7}$ | 6.7 |
| third step | $3.6\times10^{-13}$ | 12.44 |
| Pyrophosphoric acid, first step | $1.4\times10^{-1}$ | 0.85 |
| second step | $1.1\times10^{-2}$ | 1.96 |
| third step | $2.9\times10^{-7}$ | 6.54 |
| fourth step | $3.6\times10^{-9}$ | 8.44 |
| Nitrous acid | $4\times10^{-4}$ | 3.40 |
| Sulphuric acid, second step | $3\times10^{-2}$ | 1.50 |
| Sulphurous acid, first step | $1.7\times10^{-2}$ | 1.77 |
| second step | $1\times10^{-7}$ | 7 |
| Hydrogen sulphide, first step | $5.7\times10^{-8}$ | 7.24 |
| second step | $1.2\times10^{-15}$ | 14.92 |

## TABLE IV—*Continued*

| Acid | $K_a$ | $p_K(=-\log K_a)$ |
|---|---|---|
| Aliphatic Acids | | |
| Acetic acid | $1.86\times10^{-5}$ | 4.73 |
| Citric acid, first step | $8.2\times10^{-4}$ | 3.09 |
| second step | $5\times10^{-5}$ | 4.3 |
| third step | $3\times10^{-6}$ | 5.5 |
| Formic acid | $2\times10^{-4}$ | 3.7 |
| Glycine | $3.4\times10^{-10}$ | 9.37 |
| Glycollic acid | $1.52\times10^{-4}$ | 3.82 |
| Hydrogen cyanide | $7.2\times10^{-10}$ | 9.14 |
| Lactic acid | $1.55\times10^{-4}$ | 3.81 |
| Oxalic acid, first step | $3.8\times10^{-2}$ | 1.42 |
| second step | $3.5\times10^{-5}$ | 4.46 |
| Succinic acid, first step | $6.55\times10^{-5}$ | 4.18 |
| second step | $5.9\times10^{-6}$ | 5.23 |
| Tartaric acid, first step | $9.7\times10^{-4}$ | 3.01 |
| second step | $9\times10^{-5}$ | 4.05 |
| Aromatic Acids | | |
| Benzoic acid | $6.86\times10^{-5}$ | 4.16 |
| Phenol (carbolic acid) | $1.3\times10^{-10}$ | 9.89 |
| Phthalic acid, first step | $1.26\times10^{-3}$ | 2.90 |
| second step | $8\times10^{-6}$ | 5.10 |
| Picric acid | $1.6\times10^{-1}$ | 0.80 |
| Saccharin | $2.5\times10^{-2}$ | 1.40 |
| Salicylic acid | $1.06\times10^{-3}$ | 2.97 |
| Sulphanilic acid | $6.3\times10^{-4}$ | 3.2 |
| Inorganic Bases | | |
| Ammonia | $1.75\times10^{-5}$ | 4.76 |
| Hydrazine | $3\times10^{-6}$ | 5.52 |
| Aliphatic Bases | | |
| Ethylamine | $5.6\times10^{-4}$ | 3.25 |
| Diethylamine | $1.26\times10^{-3}$ | 2.90 |
| Triethylamine | $6.4\times10^{-4}$ | 3.19 |
| Glycine | $2.7\times10^{-12}$ | 11.57 |

TABLE IV—*Continued*

| Acid | $K_a$ | ($p_K = -\log K_a$) |
|---|---|---|
| Aromatic Bases | | |
| Aconitine | $1.3 \times 10^{-6}$ | 5.88 |
| Aniline | $4.6 \times 10^{-10}$ | 9.34 |
| Apomorphine | $1 \times 10^{-7}$ | 7 |
| Atropine | $4.5 \times 10^{-5}$ | 4.35 |
| Brucine, first step | $9.2 \times 10^{-7}$ | 6.04 |
| second step | $2 \times 10^{-12}$ | 11.7 |
| Cocaine | $2.6 \times 10^{-6}$ | 5.6 |
| Codeine | $9 \times 10^{-7}$ | 6.05 |
| Colchicine | $4.5 \times 10^{-13}$ | 12.35 |
| Coniine | $1.3 \times 10^{-3}$ | 2.89 |
| Ecgonine | $6 \times 10^{-12}$ | 11.22 |
| Emetine, first step | $1.7 \times 10^{-6}$ | 5.77 |
| second step | $2.3 \times 10^{-7}$ | 6.64 |
| Hydrastine | $1.7 \times 10^{-8}$ | 7.77 |
| Isoquinoline | $2 \times 10^{-9}$ | 8.7 |
| Morphine | $6.8 \times 10^{-7}$ | 6.17 |
| Narceine | $2 \times 10^{-11}$ | 10.7 |
| Narcotine | $1.5 \times 10^{-8}$ | 7.83 |
| Nicotine, first step | $7 \times 10^{-7}$ | 6.16 |
| second step | $1.4 \times 10^{-11}$ | 10.86 |
| Papaverine | $8 \times 10^{-9}$ | 8.10 |
| Physostigmine, first step | $7.6 \times 10^{-7}$ | 6.12 |
| second step | $5.7 \times 10^{-13}$ | 12.24 |
| Piperazine, first step | $6.4 \times 10^{-5}$ | 4.19 |
| second step | $3.7 \times 10^{-9}$ | 8.43 |
| Pilocarpine, first step | $7 \times 10^{-8}$ | 7.15 |
| second step | $2 \times 10^{-13}$ | 12.7 |
| Pyridine | $2 \times 10^{-9}$ | 8.7 |
| Quinine, first step | $1 \times 10^{-6}$ | 6 |
| second step | $1.3 \times 10^{-10}$ | 9.88 |
| Quinidine, first step | $3.7 \times 10^{-6}$ | 5.43 |
| second step | $1 \times 10^{-10}$ | 10 |
| Cinchonine, first step | $1.4 \times 10^{-6}$ | 5.85 |
| second step | $5 \times 10^{-11}$ | 10.3 |
| Cinchonidine, first step | $1.6 \times 10^{-6}$ | 5.80 |
| second step | $8.4 \times 10^{-11}$ | 10.08 |
| Quinoline | $3.2 \times 10^{-10}$ | 9.5 |
| Solanine | $2 \times 10^{-7}$ | 6.7 |
| Sparteine, first step | $5.7 \times 10^{-3}$ | 2.24 |
| second step | $3.1 \times 10^{-10}$ | 9.5 |
| Strychnine, first step | $1 \times 10^{-6}$ | 6 |
| second step | $2 \times 10^{-12}$ | 11.7 |

## TABLE V

### Solubility Products of Some Salts

(Averaged Values from the Literature)

| Salt | S | $p_S$ |
|---|---|---|
| Ag Salts | | |
| Inorganic | | |
| Silver | | |
| bromide | $4 \times 10^{-13}$ | 12.4 |
| bromate | $5 \times 10^{-5}$ | 4.3 |
| carbonate | $5 \times 10^{-12}$ | 11.3 |
| chloride | $1.1 \times 10^{-10}$ | 9.96 |
| chromate | $2 \times 10^{-12}$ | 11.7 |
| cyanide | $2 \times 10^{-12}$ | 11.7 |
| dichromate | $2 \times 10^{-7}$ | 6.7 |
| hydroxide | $2 \times 10^{-8}$ | 7.7 |
| iodate | $2 \times 10^{-8}$ | 7.7 |
| iodide | $1 \times 10^{-16}$ | 16 |
| sulphide | $1.6 \times 10^{-49}$ | 48.8 |
| thiocyanate | $1 \times 10^{-12}$ | 12 |
| Organic | | |
| Silver | | |
| benzoate | $9.3 \times 10^{-5}$ | 4.03 |
| oxalate | $5 \times 10^{-12}$ | 11.3 |
| salicylate | $1.4 \times 10^{-5}$ | 4.85 |
| valerianate | $8 \times 10^{-5}$ | 4.1 |
| Ba Salts | | |
| Barium | | |
| carbonate | $7 \times 10^{-9}$ | 8.16 |
| chromate | $2 \times 10^{-10}$ | 9.7 |
| iodate | $6 \times 10^{-10}$ | 9.22 |
| sulphate | $1 \times 10^{-10}$ | 10 |
| Organic | | |
| Barium | | |
| Oxalate $\cdot 3\frac{1}{2}H_2O$ | $1.7 \times 10^{-7}$ | 6.77 |
| Ca Salts | | |
| Calcium | | |
| carbonate | $1.2 \times 10^{-8}$ | 7.92 |
| fluoride | $3.5 \times 10^{-11}$ | 10.46 |
| iodate | $6.5 \times 10^{-7}$ | 6.19 |
| sulphate | $6.1 \times 10^{-5}$ | 4.22 |
| oxalate | $2 \times 10^{-9}$ | 8.7 |
| tartrate | $7.7 \times 10^{-7}$ | 6.11 |
| Cd Salts | | |
| Cadmium | | |
| sulphide | $4 \times 10^{-29}$ | 28.4 |
| oxalate | $1.1 \times 10^{-8}$ | 7.96 |

TABLE V—*Continued*

SOLUBILITY PRODUCTS OF SOME SALTS

(Average Values from the Literature)

| Salt | S | $p_s$ |
|---|---|---|
| Ce Salts | | |
| Cerium | | |
| iodate | $3.5\times10^{-10}$ | 9.46 |
| oxalate | $2.6\times10^{-29}$ | 28.39 |
| tartrate | $9.7\times10^{-20}$ | 19.01 |
| Cu Salts | | |
| Cuprous | | |
| bromide | $4.1\times10^{-8}$ | 7.39 |
| chloride | $1\times10^{-6}$ | 6 |
| iodide | $5\times10^{-12}$ | 11.3 |
| sulphide | $2\times10^{-47}$ | 46.7 |
| thiocyanate | $1.6\times10^{-11}$ ? | 10.80 ? |
| Cupric | | |
| iodate | $1.4\times10^{-7}$ | 6.85 |
| sulphide | $8.5\times10^{-45}$ | 44.07 |
| oxalate | $2.9\times10^{-8}$ | 7.54 |
| Hg Salts | | |
| Mercurous | | |
| bromide | $1.3\times10^{-21}$ | 20.89 |
| chloride | $3.1\times10^{-18}$ | 17.5 |
| iodide | $1.2\times10^{-28}$ | 27.92 |
| Mercuric | | |
| oxide | $1.4\times10^{-26}$ | 25.9 |
| sulphide | $4\times10^{-53}$ | 52.4 |
| K Salts | | |
| Potassium | | |
| bitartrate | $3\times10^{-4}$ | 3.5 |
| La Salts | | |
| Lanthanum | | |
| iodate | $5.9\times10^{-10}$ | 9.23 |
| oxalate | $2\times10^{-28}$ | 27.7 |
| tartrate | $2\times10^{-19}$ | 18.7 |
| Mg Salts | | |
| Magnesium | | |
| carbonate | $2\times10^{-4}$ | 3.7 |
| fluoride | $7\times10^{-9}$ | 8.16 |
| hydroxide | $1.2\times10^{-11}$ | 10.92 |
| ammonium phosphate | $2.5\times10^{-13}$ | 12.6 |
| oxalate | $8.6\times10^{-5}$ | 4.07 |

## TABLE V—*Continued*

### SOLUBILITY PRODUCTS OF SOME SALTS

(Average Values from the Literature)

| Salt | S | $p_s$ |
|---|---|---|
| Pb Salts | | |
| Lead | | |
| carbonate | $3.3 \times 10^{-14}$ | 13.48 |
| chromate | $1.8 \times 10^{-14}$ | 13.75 |
| fluoride | $7 \times 10^{-9}$ | 7.5 |
| iodate | $1.2 \times 10^{-13}$ | 12.92 |
| iodide | $1.3 \times 10^{-8}$ | 7.5 |
| sulphate | $1 \times 10^{-8}$ | 8 |
| sulphide | $1 \times 10^{-29}$ | 29 |
| oxalate | $3.4 \times 10^{-11}$ | 10.47 |
| Sr Salts | | |
| Strontium | | |
| carbonate | $1.6 \times 10^{-9}$ | 8.80 |
| sulphate | $2.8 \times 10^{-7}$ | 6.56 |
| oxalate | $5 \times 10^{-8}$ | 7.3 |
| Tl Salts | | |
| Thallium | | |
| bromide | $2 \times 10^{-6}$ | 5.7 |
| bromate | $8.5 \times 10^{-5}$ | 4.07 |
| chloride | $1.5 \times 10^{-4}$ | 3.82 |
| iodate | $2.2 \times 10^{-6}$ | 5.66 |
| iodide | $2.8 \times 10^{-8}$ | 7.55 |
| sulphide | $4.5 \times 10^{-23}$ | 22.35 |

## TABLE VI

### SOME COMPLEX CONSTANTS

| Expression | Value of K | Expression | Value of K |
|---|---|---|---|
| $\frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$ | $6.8 \times 10^{-8}$ | $\frac{[Hg^{++}][Cl^-]^4}{[HgCl_4^=]}$ | $6 \times 10^{-17}$ |
| $\frac{[Ag^+][NO_2^-]^2}{[Ag(NO_2)_2^-]}$ | $1.5 \times 10^{-3}$ | $\frac{[Hg^{++}][Br^-]^4}{[HgBr_4^=]}$ | $2.2 \times 10^{-22}$ |
| $\frac{[Ag^+][S_2O_3^=]^2}{[Ag(S_2O_3)_2^{\equiv}]}$ | $1 \times 10^{-13}$ | $\frac{[Hg^{++}][I^-]^4}{[HgI_4^=]}$ | $5 \times 10^{-31}$ |
| $\frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]}$ | $1 \times 10^{-21}$ | $\frac{[Hg^{++}][CN^-]^4}{[HgCN_4^=]}$ | $4 \times 10^{-42}$ |
| $\frac{[Cu^+][CN^-]^4}{[Cu(CN)_4^{\equiv}]}$ | $5 \times 10^{-28}$ | | |
| $\frac{[HgCl_2][Cl^-]^2}{[HgCl_4^=]}$ | $1 \times 10^{-2}$ | $\frac{[Hg^{++}][CNS^-]^4}{[Hg(CNS)_4^=]}$ | $1 \times 10^{-22}$ |

## TABLE VII

### List of Rational Atomic Weights (1925)

| Element | Symbol | International Atomic Weight, 1925 | Atomic Weight in Air. (Rational Atomic Weight) | Atomic Weight in Air, Approximate to 0.1 Per Cent |
|---|---|---|---|---|
| Aluminum | Al | 26.97 | *26.96* | 27 |
| Antimony | Sb | 121.77 | *121.765* | 121.8 |
| Arsenic | As | 74.96 | *74.95* | 75 |
| Barium | Ba | 137.37 | *137.37* | 137.4 |
| Bismuth | Bi | 209 | *209.01* | 209 |
| Boron | B | 10.82 | *10.81* | 10.8 |
| Bromine | Br | 79.916 | *79.90* | 79.9 |
| Cadmium | Cd | 112.41 | *112.41* | 112.4 |
| Calcium | Ca | 40.07 | *40.06* | 40.1 |
| Carbon | C | 12 | *11.995* | 12 |
| Cerium | Ce | 140.25 | *140.25* | 140.2 |
| Chlorine | Cl | 35.457 | *35.45* | 35.45 |
| Chromium | Cr | 52.01 | *52.01* | 52 |
| Cobalt | Co | 58.94 | *58.94* | 58.9 |
| Copper | Cu | 63.57 | *63.57* | 63.6 |
| Fluorine | F | 19 | *18.99* | 19 |
| Gold | Au | 197.2 | *197.22* | 197.2 |
| Hydrogen | H | 1.008 | *1.001* | 1 |
| Iodine | I | 126.932 | *126.912* | 127 |
| Iron | Fe | 55.84 | *55.84* | 55.8 |
| Lead | Pb | 207.20 | *207.21* | 207.2 |
| Lithium | Li | 6.940 | *6.940* | 6.94 |
| Magnesium | Mg | 24.32 | *24.32* | 24.3 |
| Manganese | Mn | 54.93 | *54.93* | 54.9 |
| Mercury | Hg | 200.61 | *200.62* | 200.6 |
| Molybdenum | Mo | 96 | *96* | 96 |
| Nickel | Ni | 58.69 | *58.69* | 58.7 |
| Nitrogen | N | 14.008 | *13.998* | 14 |
| Oxygen | O | 16 | *15.995* | 16 |
| Palladium | Pd | 106.7 | *106.7* | 106.7 |
| Phosphorus | P | 31.027 | *31.015* | 31 |
| Platinum | Pt | 195.23 | *195.24* | 195.2 |
| Potassium | K | 39.096 | *39.076* | 39.1 |
| Selenium | Se | 79.2 | *79.2* | 79.2 |
| Silicon | Si | 28.06 | *28.05* | 28 |
| Silver | Ag | 107.880 | *107.88* | 107.9 |
| Sodium | Na | 22.997 | *22.99* | 23 |
| Strontium | Sr | 87.63 | *87.62* | 87.6 |
| Sulphur | S | 32.064 | *32.049* | 32 |
| Thallium | Tl | 204.39 | *204.39* | 204.4 |
| Tin | Sn | 118.70 | *118.70* | 118.7 |
| Titanium | Ti | 48.1 | *48.1* | 48.1 |
| Tungsten | W | 184 | *184* | 184 |
| Uranium | U | 238.17 | *238.17* | 238.2 |
| Vanadium | V | 50.96 | *50.96* | 51 |
| Zinc | Zn | 65.38 | *65.38* | 65.4 |

*Explanation of the Table.*—The third column contains the international atomic weights, 1925, published in the second report of the International Committee on Chemical Elements. (J. Am. Chem. Soc., 47, 600 (1925)).

These atomic weights are referred to weighings *in vacuo.* They should not be used for accurate analytical work unless a correction is applied for the buoyant effect of air. This correction has been calculated by N. Schoorl, by taking into consideration the atomic volume of each element. (Chem. Weekblad, **15**, 547 (1918); **22**, 156 (1925); Z. analyt. Chem., **57**, 209 (1918)). The fourth column contains this corrected list of *rational atomic weights*, which must be used in accurate quantitative work.

In ordinary quantitative work the atomic weights which are listed in the fifth column may be used. They are approximated to 0.1 per cent.

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